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(54) Title: COMPOSITE THERMOPLASTIC POLYMERS BASED ON REACTION WITH BIORENEWABLE OILS

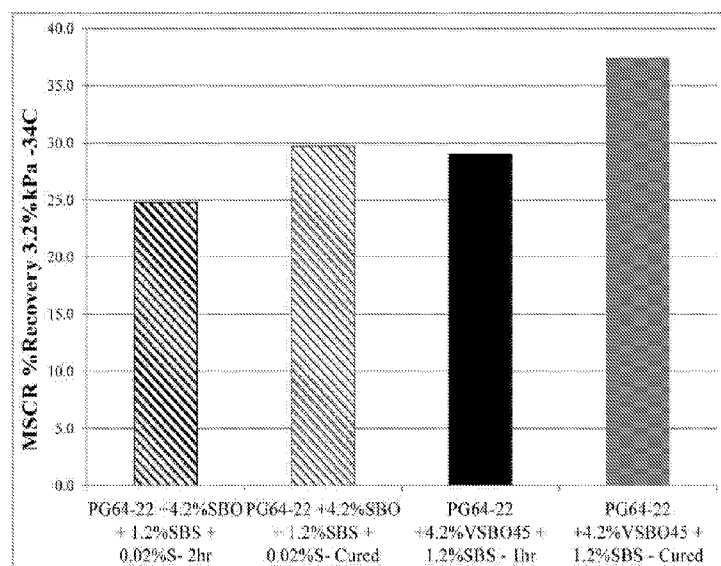


Figure 1

(57) Abstract: Provided herein is a polymeric composition, comprising a random copolymer comprising three or more distinct monomers, wherein a first monomer is a biorenewable oil and at least one monomer has been polymerized into a thermoplastic polymer. Also provided herein is a modified asphalt for use in several asphalt end-use applications, comprising an asphalt binder in an amount ranging from about 60-99.9 wt%, an asphalt modifier in an amount ranging from about 0.1-40 wt%, wherein the asphalt modifier comprises about 1-75 wt% of a thermoplastic polymer and a remaining balance of biorenewable oil.

COMPOSITE THERMOPLASTIC POLYMERS BASED ON REACTION WITH BIORENEWABLE OILS

TECHNICAL FIELD

[0001] This disclosure relates to reacted and unreacted biorenewable oil in combination with thermoplastic polymer products that are mixed into asphalt to enhance performance of virgin asphalt and/or pavements containing recycled and/or aged bituminous material.

BACKGROUND

[0002] Recent technical challenges facing the asphalt industry have created opportunities for the introduction of agriculture-based products for the overall performance enhancement of asphalt. Although thermoplastic polymers and waxes have been used in asphalt as modifiers to improve various aspects of performance, interesting synergistic benefits from the use of composite modifiers containing thermoplastic polymers and bio-renewable oil based products can lead to useful performance enhancements. Such performance enhancements may include for example but aren't limited to expanding the useful temperature index (UTI) of asphalt, rejuvenating aged asphalt while improving durability and toughness, and compaction aid applications in which the product can be used to reduce the required compaction energy and/or haul distance of the asphalt loose mix from the plant to the job-site.

SUMMARY

[0003] Provided herein is a polymeric composition, comprising three or more distinct monomers that leads to the formation of a random copolymer, wherein at least one monomer is a biorenewable oil and at least one monomer has been polymerized into a thermoplastic polymer.

[0004] Also provided herein is a modified asphalt for use in several asphalt end-use applications, comprising an asphalt binder in an amount ranging from about 60-99.9 wt%, an asphalt modifier in an amount ranging from about 0.1-40 wt%, wherein the asphalt modifier comprises about 1-75 wt% of a thermoplastic polymer and a remaining balance of biorenewable oil.

FIGURES

[0005] Figure 1 shows a comparison of the results of Example 1 in terms of percent of recoverable strain (%Recovery) after a 1 sec 3.2kPa creep loading using the Multiple Stress Creep and Recovery Procedure (MSCR) procedure after blending and after full curing for 12 hrs.

[0006] Figure 2 shows a comparison of the results of Example 2 in terms of percent of recoverable strain (%Recovery) after a 1 sec 3.2kPa creep loading using the Multiple Stress Creep and Recovery Procedure (MSCR) procedure after blending and after full curing for 12 hrs.

[0007] Figure 3 shows a comparison of the results of Example 3 in terms of percent of recoverable strain (%Recovery) after a 1 sec 3.2kPa creep loading using the Multiple Stress Creep and Recovery Procedure (MSCR) procedure after blending and after full curing for 12 hrs.

[0008] Figure 4 shows a comparison of the results of Example 4 in terms of percent of recoverable strain (%Recovery) after a 1 sec 3.2kPa creep loading using the Multiple Stress Creep and Recovery Procedure (MSCR) procedure after blending and after full curing for 12 hrs.

[0009] Figure 5 provides results of Example 4 in terms of percent of recoverable strain (%Recovery) after a 1 sec 3.2kPa creep loading using the Multiple Stress Creep and Recovery Procedure (MSCR) procedure, plotted against process time (Blending/Curing).

[0010] Figure 6 shows a comparison of the results of Example 5 in terms of percent of recoverable strain (%Recovery) after a 1 sec 3.2kPa creep loading using the Multiple Stress Creep and Recovery Procedure (MSCR) procedure after blending and after full curing for 12 hrs.

[0011] Figure 7 shows a comparison of the results of Example 6 in terms of percent of recoverable strain (%Recovery) after a 1 sec 3.2kPa creep loading using the Multiple Stress Creep and Recovery Procedure (MSCR) procedure after blending and after full curing for 12 hrs.

[0012] Figure 8 shows a comparison of the results of Example 7 in terms of percent of recoverable strain (%Recovery) after a 1 sec 3.2kPa creep loading using the Multiple Stress Creep and Recovery Procedure (MSCR) procedure after blending and after full curing for 12 hrs.

[0013] Figure 9 shows the specific heat of the asphalt modifier described in Example 8.

[0014] Figure 10 shows a plot of the complex modulus against temperature for asphalt modified with the asphalt modifiers described in Example 9. Results show three temperature ranges of asphalt performance in terms of modifier functionality and desired performance.

[0015] Figure 11 shows the specific heat of the asphalt modifier described in Example 10, measured using a Perkin Elmer DSC during a heating ramp at a fixed heating rate of 10°C/min.

[0016] Figure 12 shows a plot of the complex viscosity against temperature for asphalt modified with the asphalt modifiers described in Example 10.

[0017] Figure 13 shows a plot of the complex viscosity against temperature for asphalt modified with the asphalt modifiers described in Example 11.

DETAILED DESCRIPTION

[00018] Aspects described herein provide an asphalt modifier system comprising a biorenewable oil-based product and a thermoplastic polymer or wax (also referred to herein as “asphalt modifier,” a “blend,” a “thermoplastic polymer and oil blend,” a “modifier system”, etc.). Methods of manufacturing the modifier system as well as its incorporation into asphalt, roofing, and coating applications are also described.

[00019] “Acid value” is defined as mass of potassium hydroxide needed in mg to neutralize one gram of sample according to AOCS Cd 3d-63. Acid value is a way of quantifying the amount of free fatty acid in a sample and has the units mg KOH/g.

[00020] “Amine value” is defined as the number of mg KOH equivalent to the basicity of one gram of test sample and has the units mg KOH/g.

[00021] “Oligomer” is defined as a polymer having a number average molecular weight (Mn) larger than 1000. A “monomer” makes up everything else and includes monoacylglycerides (MAG), diacylglycerides (DAG), triacylglycerides (TAG), and free fatty acids (FFA).

[00022] “Reacted” blends refer to blends in which sulfur crosslinking and polymerization occurred prior to asphalt addition.

[00023] “Unreacted” blends refer to blends in which no sulfur crosslinking or polymerization occurred prior to asphalt addition.

[00024] Also, for purposes herein, it shall be understood that vulcanization and sulfurization are used herein interchangeably.

Biorenewable Oil

[00025] As used herein, “biorenewable oils” can include oils isolated from plants, animals, and microorganisms including algae.

[00026] Examples of plant-based oils that may be used include but are not limited to soybean oil, linseed oil, canola oil, rapeseed oil, cottonseed oil, sunflower oil, palm oil, tall oil, peanut oil, safflower oil, corn oil, corn stillage oil (also known as recovered corn oil) and corresponding distillates and fatty acids, lecithin (phospholipids) and combinations and crude streams thereof or co-products, by-products, or residues resulting from oil refining processes.

[00027] Examples of animal-based oils may include but are not limited to animal fat (e.g., lard, tallow), and combinations and crude streams thereof.

[00028] Biorenewable oils can also include partially and fully hydrogenated oils, oils with conjugated bonds, and bodied oils wherein a heteroatom is not introduced, including, diacylglycerides, monoacylglycerides, free fatty acids, and alkyl esters of fatty acids (e.g., methyl, ethyl, propyl, and butyl esters).

[00029] Biorenewable oils can also include derivatives thereof, for example, previously modified, radically polymerized, polymerized, or functionalized oils (intentional or unintentional) wherein a heteroatom (oxygen, nitrogen, sulfur, and phosphorus) has been introduced may also be used as the starting oil material. Examples of unintentionally modified oils are used cooking oil, trap grease, brown grease, or other used industrial oils. Examples of previously modified oils are those that have been previously vulcanized or polymerized by other polymerizing technologies, such as maleic anhydride or acrylic acid modified, hydrogenated, dicyclopentadiene modified, conjugated via reaction with iodine, interesterified, or processed to modify acid value, hydroxyl number, or other properties. Such modified oils can be blended with unmodified plant-based oils or animal-based oils, fatty acids, glycerin, and/or gums materials.

[00030] In preferred aspects, the biorenewable oil is recovered corn oil (typically residual liquids resulting from the manufacturing process of turning corn into ethanol) or soybean oil. In another preferred aspect, the biorenewable oil is a free fatty acid. One skilled in the art will recognize that if higher functionality is desired, biorenewable oils having higher levels of unsaturation may be used. Conversely, higher saturates may be incorporated to further vary solvent parameters of the polymerized oils to improve performance properties in asphalt.

Thermoplastic Polymer

[00031] As used herein "thermoplastic polymers" may include polymers commonly classified as "elastomers" and "plastomers," pre-polymers (such as thermoplastic resins), oligomers, and high molecular weight polymers. In one preferred aspect the thermoplastic polymer can be a polyolefin or a modified polyolefin. In other preferred aspects, a styrene-based elastomer is used. In other aspects the thermoplastic polymer may be that which is contained in ground tire rubber (GTR). Examples of useful thermoplastic polymers for this application are styrene, divinylbenzene, indene, or other vinyl aromatics, including styrene-based polymers such as styrene-butadiene-styrene (SBS) produced by Kraton and Dynasol, and emulsified or non-emulsified styrene-butadiene rubber; Reacted Elastomeric Terpolymers such as the ElvaloyTM RET produced by DuPont; and polyolefins such as polyethylene, polypropylene, and

polybutylene, and functionalized polyolefin such as the TitanTM plastomer produced by Honeywell.

[00032] As described above, “thermoplastic polymers” may also include waxes such as polyamide waxes that comprise a polyamine and a fatty acid, such as ethylene bistearamide and tristearamide.

Asphalt Modifier System

[00033] The asphalt modifier system described herein comprises a blend of biorenewable oil and a thermoplastic polymer. Modifier systems in the prior art do not blend biorenewable oil with a thermoplastic polymer but rather directly add thermoplastic polymer to asphalt without additional materials or components. It has been found that the blend of the present invention and its composition accelerates dispersion and provides more uniformity when incorporated into asphalt, even with lower shearing and blending time requirements compared to that used in prior art systems.

[00034] In conventional polymer modified asphalt (the prior art), the asphalt is heated to temperatures often exceeding 180°C at which point the polymer is added to the asphalt at the desired dosage. Since the polymer is often provided in solid pellets, a lengthy high temperature and high shear blending period is required to homogeneously distribute the polymer in the asphalt. For many styrene-based elastomeric modifiers, a second step is included in the prior art during which a cross-linker such as peroxide or a sulfur containing compound is added to the blend and reacted for a few hours. Finally the asphalt along with the polymer continues to be heated for an additional 12-15 hours to ensure full curing of the polymer, during which the polymer swells through adsorption of lighter fractions in the asphalt.

[00035] The described modifier system herein provides a polymer with enhanced performance characteristics (in terms of elasticity and modulus) but with higher workability, and in some cases, lower melting points. This enables the use of a lower blending temperature, shorter blending times, and lower agitation levels if necessary. Furthermore, the composite thermoplastic polymer described herein often do not require lengthy “curing” periods to achieve equal or better performance characteristics than that of conventional thermoplastic polymers added using conventional methodology.

[00036] The blend of the present invention can be achieved through direct reaction of a thermoplastic polymeric material into a suitable, and in some aspects, reactive biorenewable oil. The blend often times comprises between about 1-75 wt% of a thermoplastic polymer with the

remaining balance being biorenewable oil. The upper limit of the polymer is defined by the target end-use asphalt application. Lower thermoplastic polymer dosages are used in cases when the end-use application requires higher workability or reduction of production temperatures. Furthermore, depending on the end-use application, one may control the degree of incorporation of the biorenewable oil into the thermoplastic polymer. For example, in the case of asphalt modification, addition of the reactive polymerized biorenewable oils to the asphalt prior to addition of the thermoplastic polymer results in an in-situ polymerization and reaction in the asphalt. In other examples, the degree of crosslinking in the thermoplastic polymer may be manipulated by controlling the level of crosslinker incorporated into the crosslinked biorenewable oil. The following paragraphs describe various aspects of this invention.

[00037] Generally, the process to manufacture the asphalt modifier system of the present invention comprises first heating a biorenewable oil to a sufficiently high temperature. This temperature is in the range of 80 to 150°C for a suitable waxy or crystalline polymers or polyolefin (a suitable polyolefin will have a melting point above the pavement performance temperature range and below that of typical production temperatures). For amorphous polymers such as styrene based elastomers, the desired temperature will be at or higher than the glassy or rubbery transition, or a temperature sufficient enough to achieve a reduction in cohesive forces for efficient distribution in the oil medium. In cases where a reactive biorenewable oil is used, the temperature should be sufficiently high for the reactivity between the biorenewable oil and the thermoplastic polymer. The thermoplastic polymer is gradually added while maintaining the temperature of the blend and agitated until a uniform, homogenized distribution in the biorenewable oil medium is achieved.

[00038] Blending time is defined as the time required for homogenizing the polymer into the biorenewable oil. This will often occur within 1 hour without the need for high shear agitation. For polymers such as styrene-butadiene block copolymers, high shear blending may be used to accelerate the rate of polymer incorporation into the biorenewable oil, but is not required.

[00039] For polymers such as styrene-butadiene block copolymers, a period of high temperature curing may facilitate the swelling of the thermoplastic polymer through absorption of fractions in the biorenewable oil, resulting in improved elasticity and an increase in modulus, especially when used in asphalt end use applications.

[00040] In another aspect, the thermoplastic polymer may have a high wax content or crystalline fraction. In preferred embodiments, the wax has a melting temperature higher than typical asphalt end-use performance temperatures (usually about 80°C) but lower than typical

production and construction temperatures (usually about 135°C). This leads to a reduction in viscosity in the end use application when it is heated beyond the melting point, enabling the reduction of required production and construction temperatures. Polyolefins such as polyethylene, polypropylene, and polybutylene are well suited to this application.

[00041] In another aspect, the modifier system of the present invention may further include a crosslinking agent such as sulfur-containing compounds or peroxides added after the homogenization of the polymer in the biorenewable oil. Another crosslinking agent that may be used is a sulfur-containing compound in combination with a peroxide, polyphosphoric acid, and super acid catalysts.

[00042] The crosslinker may be fully or partially reacted with the thermoplastic polymer and the biorenewable oil, depending on the stage at which the crosslinker is added to the blend, and the reaction time. Fully crosslinking can provide a continuous network of the elastomeric polymers across the biorenewable oil medium that will lead to enhanced mechanical, rheological, and damage resistance properties as needed in asphalt applications and specifications.

[00043] In another aspect, the cross linker is added to the biorenewable oil before or at the time of the addition of the thermoplastic polymer.

[00044] In another aspect for asphalt applications, the crosslinker is not added to the oil and polymer reaction, but is instead added to the asphalt blend comprising the blend for an in-situ reaction with the thermoplastic polymer-oil blend. Sufficient blending temperatures and reaction time would be required for full reaction. Effectiveness of the reaction in asphalt is often assessed by measurement of the elasticity of the binder with a Dynamic Shear Rheometer, as shown in the examples.

[00045] In another aspect, a reactive biorenewable oil, preferably at least a partially sulfurized biorenewable oil may be used, which contains reactive sulfur when heated to sufficiently high temperatures (about 100 to 200°C, but preferably between 185 to 195°C). Addition of a thermoplastic polymer with sufficient unsaturation can lead to reaction with the reactive sulfur in the oil resulting in crosslinks of the reactive double bonds in the polymerized oil (may be in the free fatty acid, MAG, DAG, TAG, or any oligomer thereof), and the thermoplastic polymer as well as between molecules of the thermoplastic polymer. This will result in an extremely stable combined modifier system as well as improved mechanical, rheological, and damage resistance properties. Thermoplastic elastomers such as styrene-butadiene-styrene are well suited for such an application.

[00046] The reaction between the biorenewable oil, thermoplastic polymer, and optional crosslinking agent continues until desired physical properties are met. For asphalt modification, it is desired to maximize the elasticity (e.g. as measured using the DSR Multiple Stress Creep and Recovery procedure) by increasing the degree of polymerization, while maintaining the workability of the resulting thermoplastic polymer at temperatures lower than 190°C to enable efficient blending in the asphalt media which will place a limit on the desired degree of polymerization.

Exemplary Embodiments

[00047] For a better understanding of the various embodiments described above, a few exemplary embodiments are hereinafter described. The most preferred aspect includes reacting vulcanized biorenewable oil (wherein the biorenewable oil is vulcanized using sulfur as described in co-pending provisional patent application number 62/126,064) with the thermoplastic polymer before incorporating the blend into asphalt. Another preferred aspect is incorporating the biorenewable oil and the thermoplastic polymer directly and individually (i.e., without reacting) into the asphalt and optionally incorporating a sulfur crosslinker thereafter. Another preferred aspect is incorporating both vulcanized biorenewable oil and the thermoplastic polymer directly and individually into asphalt wherein the vulcanized biorenewable oil acts as a cross-linker carrier.

[00048] As can be gleaned from the above description and the examples below, the asphalt modifier system - comprises a combination of 3 or more monomers that lead to the formation of random copolymers, wherein the random copolymers include biorenewable oils that have been cationically polymerized using Bronsted acids and Lewis acids, including super acid catalysis, or sulfurization techniques. One of skill in the art will also realize that the use of natural oils, which consist of fatty acids possessing monounsaturated and polyunsaturated fatty acids, lead to the formation of hyperbranched polymers.

End-Use Applications

[00049] For the purpose of this invention, asphalt, asphalt binder, and bitumen refer to the binder phase of an asphalt pavement. Bituminous material may refer to a blend of asphalt binder and other material such as aggregate or filler. The binder used in this invention may be material acquired from asphalt producing refineries, flux, refinery vacuum tower bottoms, pitch, and other residues of processing of vacuum tower bottoms and solvent de-asphalting processes, as well as

oxidized and aged asphalt from recycled bituminous material such as reclaimed asphalt pavement (RAP), and recycled asphalt shingles (RAS).

[00050] In one aspect, the present invention provides a modified asphalt comprising a blend of 60 wt% to 99.9 wt% of asphalt binder and 0.1 wt% to 40 wt% of the asphalt modifier. The modified asphalt may be used for road paving or roofing applications. Additionally, modified asphalt can be used in a variety of industrial applications, not limited to coatings, drilling applications, and lubricants.

[00051] In another aspect, the present invention provides a modified asphalt comprising a blend of 60 wt% to 99.9 wt% asphalt binder and 0.1 wt% to 40 wt% of the asphalt modifier, and one or more of the biorenewable oils described above, for example: unmodified plant-based oil, animal-based oil, fatty acids, fatty acid methyl esters, gums or lecithin, and gums or lecithin in modified oil or other oil or fatty acid.

[00052] Other components, in addition to the asphalt modifier described in this invention, may be combined with the asphalt binder to produce a modified asphalt, for example but not limited to, thermoplastic elastomeric and plastomeric polymers (styrene butadiene styrene, emulsified or non-emulsified styrene-butadiene rubber, ethylene vinyl acetate, functionalized polyolefins, etc.), polyphosphoric acid, anti-stripping additives (amine-based, phosphate-based, etc.), warm mix additives, emulsifiers, and fibers. Typically, these components are added to the asphalt binder/polymerized oil at doses ranging from about 0.1 wt% to about 10 wt%.

Asphalt Modification

[00053] The declining quality of bitumen drives the need for adding chemical modifiers to enhance the quality of asphalt products. Heavy mineral oils from petroleum refining are the most commonly used modifiers.

[00054] Mineral flux oils, petroleum-based crude distillates, and re-refined mineral oils have been used in attempts to soften the asphalt. Often, use of such material results in a decrease of the high temperature modulus of asphalt more than the low temperature, making the asphalt more prone of rutting at high temperatures. Such effects result in the reduction of the Useful Temperature Index (UTI).

[00055] Mineral flux oils, petroleum-based crude distillates, and re-refined mineral oils often have volatile fractions at pavement construction temperatures (e.g., 150 to 180°C), generally have lower flashpoints than that of asphalt, and may be prone to higher loss of performance due to oxidative aging.

[00056] The thermoplastic polymer and oil blends described herein are not only viable substitutes for mineral oil, but have also been shown to extend the UTI of asphalts to a greater degree than other performance modifiers, therefore providing substantial value to asphalt manufacturers. The observed increase in UTI using the blends described herein is a unique property not seen in other asphalt softening additives such as asphalt flux, fuel oils, products based on aromatic or naphthenic distillates, or flush oils. Typically one grade improvement in either the SHRP Performance Grading (PG) specification or the Penetration grading system used in many countries is achieved with approximately 2 to 3 wt% of the blend by weight of the asphalt. For example, the increase in UTI seen for approximately 3% by weight addition of the asphalt modifier can be as much as 4°C, therefore providing a broader PG modification range such that the lower end temperature can be lower without sacrificing the higher end temperature.

Rejuvenation of Aged Bituminous Material

[00057] Asphalt “ages” through a combination of mechanisms, mainly oxidation and volatilization. Aging increases asphalt modulus, decreases viscous dissipation and stress relaxation, and increases brittleness at lower performance temperatures. As a result, the asphalt becomes more susceptible to cracking and damage accumulation. The increasing usage of recycled and reclaimed bituminous materials which contain highly aged asphalt binder from sources such as reclaimed asphalt pavements (RAP) and recycled asphalt shingles (RAS) have created a necessity for “rejuvenators” capable of partially or completely restoring the rheological and durability of the aged asphalt. The use of the thermoplastic polymer and oil blends described herein are particularly useful for RAP and RAS applications as they combine the rejuvenating effect of the oil component with the toughening effect of the thermoplastic polymer incorporated into the blend.

[00058] Accordingly, the thermoplastic polymer and oil blends described herein have been shown to be capable of rejuvenating and toughening the aged asphalt binder, and restoring the rheological properties of a lesser aged asphalt and enhancing the durability of the binder. As a result, small dosages of the blend can be used to incorporate high content of aged recycled asphalt material into pavements and other applications resulting in significant economic saving and possible reduction in the environmental impact of the pavement through reduction of use of fresh resources.

Replacing Conventional Use of Thermoplastic Polymer in Asphalt

[00059] Asphalt is often modified with thermoplastic elastomeric and plastomeric polymers such as Styrene-Butadiene Styrene (SBS) as well as ground tire rubber to increase high temperature modulus and elasticity, to increase resistance to heavy loading and toughening the asphalt matrix against damage accumulation through repetitive loading, either through traffic on pavements, or environmental and thermal effects in roofing applications. Such polymers are usually used at 3 to 7 wt% dosages in the asphalt and can be as high as 20% for ground tire rubber.

[00060] Conventionally the polymer is high shear blended directly into asphalt at temperatures often exceeding 180°C and allowed to “cure” at similar temperatures during which the polymer swells by adsorption of lighter fractions in the asphalt until a continuous volume phase is achieved in the asphalt.

[00061] The volume phase of the fully cured polymer will be affected by degree of compatibility of the polymer in the asphalt and the fineness of the dispersed particles, resulting in an increased specific area and enhanced swelling potential through increase of the interface surface between asphalt and polymer.

[00062] The thermoplastic polymer and oil blends described herein can be added directly to the asphalt to achieve superior mechanical and rheological properties due to the higher polymer dispersion and compatibilization in the oil medium and consequently a more efficient network formation in the asphalt compared to the conventionally used thermoplastic polymers.

[00063] Furthermore, the thermoplastic polymer and oil blend does not require lengthy blending time or curing periods after adding to the asphalt to achieve and exceed the mechanical properties of asphalt blends made using the conventional polymer modification method described in above.

Compaction Aid Additives for use in Asphalt

[00064] Asphalt pavements require a minimum amount of energy to be produced and compacted. This energy is provided through a combination of heat and mechanical energy through use of roller compactors. Thus additives allowing for reduction in the required compaction energy to achieve target mixture density can enable a reduction of the compactor passes or the temperature, thus enabling an increase in the maximum haul distance of the asphalt mixture from the plant to the job site.

[00065] The different mechanisms through which such compaction aid additives function may include increased lubrication of aggregates during asphalt mixture compaction, reduction of

the binder viscosity at production temperatures, and better coating and wettability of the aggregates.

[00066] The thermoplastic polymer and oil blends described herein can be used as a compaction aid, to achieve a decrease in the required compaction energy through increase in aggregate lubrication and aggregate wettability, as well as decrease in viscosity at the higher temperatures used during construction when the thermoplastic polymer has a melting point in the range of 80 to 135°C (example of which is a suitable polyolefin such as polyethylene, oxidized polyethylene, polypropylene, and polybutylene). In such an application the additive would be used at dosages preferably in the range of between about 0.1 and 2% by weight of the bitumen.

EXAMPLES

[00067] For purposes herein, natural oil-based “oligomer” is defined as a polymer having a number average molecular weight (M_n) larger than 1000. A monomer makes up everything else and includes monoacylglycerides (MAG), diacylglycerides (DAG), triacylglycerides (TAG), and free fatty acids (FFA). Molecular weight is determined using Gel Permeation Chromatography techniques.

Example 1: Use of Sulfurized Vegetable-Based Oil as Polymer Compatibilizer and Cross-Linker

[00068] Two polymer modified asphalt blends were compared, one in which elemental sulfur was added directly to the asphalt to cross link the SBS following a conventional asphalt polymer modification procedure (Blend A), and the other in which a sulfurized vegetable based oil with no cross linker was added to the asphalt before the addition of the SBS (Blend B).

[00069] The Multiple Stress Creep and Recovery procedure under AASHTO T350 is a procedure designed for measuring the Elasticity of asphalt binders through repeated 1 sec creep and 9 sec recovery steps. This procedure is especially useful for assessing the performance of polymer modified asphalt. Using the strain response from the creep and recovery steps a percent recovery (%R) is calculated as a measure of the ratio of the recoverable strain during the 9 sec recovery period to the total strain imposed by the end of the 1 sec creep step. By normalizing the strain at the end of the creep period to the imposed stress a compliance value can be measured (J). The compliance corresponding to the remaining strain at the end of the recovery period is referred to as the non-recoverable compliance (J_{nr}). An effective elastomeric modifier would increase the % Recovery and decrease the J_{nr} .

[00070] Blend A is a modified asphalt binder comprising:

- 94.58% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.

- 4.2% of refined soy bean oil by weight of the blend.
- 1.2% of Styrene-Butadiene Styrene (Kraton D-1192) by weight of the blend.
- 0.02% of elemental sulfur by weight of the blend.

[00071] Blend B is a modified asphalt binder comprising:

- 94.6% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 4.2% of a polymerized vegetable-based oil, as described below:
 - 60% by weight of a sulfurized refined soy bean oil reacted with 7.0% by weight of elemental sulfur at 175°C for 33 hrs under a Nitrogen sparge. This resulted in a modifier with 70.0% oligomers. It will be hereby referred to as VSBO70.
 - 40% by weight of refined soy bean oil
 - Blend of VSBO70 and the unmodified oil had a 45% oligomer content. It will be hereby referred to as VSBO45.
- 1.2% of Styrene-Butadiene Styrene (Kraton D-1192) by weight of the blend.

Blending Procedure:

1. The oil was blended into the asphalt after the binder had been annealed at 150°C for 1 hour. The modified binder heated to about 193°C for polymer modification.
2. The RPM in the high shear mixer was set to 1000 while the SBS was added (within 1 minute). Immediately after addition of the polymer the RPM was briefly ramped up to 3000 rpm for approximately 10 minutes to insure full break down of the SBS pellets, after which the shear level was lowered to 1000 rpm.
3. Polymer blending was continued at 1000 rpm for a total of 2 hrs.
4. If a cross linker step is needed, the temperature was dropped to about 182°C at a 150 rpm at which point the sulfur cross linker was added. Blending was continued at 182°C and 150 rpm for 2 hrs.
5. Samples were taken from the Polymer modified binder before and after it was placed in an oven at 150°C for curing for approximately 12 hrs (overnight) to achieve full swelling of the polymer.

[00072] Performance grade tests were performed in accordance to AASHTO M320. Multiple Stress Creep and Recovery tests were performed on the unaged binder at 34°C in accordance to AASHTO T350. Details are shown in Table 1:

Table 1

Binder Name	Blend Conditions				J_{br} at 34°C, 3.2 kPa	%Recovery at 34°C, 3.2 kPa
	Cross- linker Added	12hr Curing	Blend Time	SBS/Oil Ratio		
PG64-22 +4.2%SBO + 1.2%SBS + 0.02%S	Yes	No	4 hours	0.22	0.15	24.78
	Yes	Yes		0.22	0.122	29.72
PG64-22 +4.2%VSBO45 + 1.2%SBS	No	No	1 hour	0.22	0.128	28.97
	No	Yes		0.22	0.105	37.44

[00073] The results show that not only did use of the sulfurized vegetable based oil eliminate the need for a cross-linker by delivering superior elasticity and compliance at the conclusion of blending, it also developed a more efficient and higher elasticity elastomeric polymer compared to the binder that did not contain the sulfurized modifier at the conclusion of the curing step. This can significantly simplify the modification process for the end user, as handling of elemental sulfur and addition of a cross-linking step is unnecessary. As a result of eliminating the crosslinking step the blend time was significantly reduced from 4 hrs to 1 hr.

[00074] By comparing the results of Blend B to that of the conventional blend (Blend A) it is observed that the use of the reactive sulfurized oil eliminated the need for the 12 hr curing period by delivering nearly equal performance after only 1 hr of blending.

Example 2: Use of sulfurized vegetable-based oil as polymer compatibilizer and cross-linker:

[00075] Two polymer modified asphalt blends were compared, one in which elemental sulfur was added directly to the asphalt to cross link the SBS following a conventional asphalt polymer modification procedure (Blend A), and the other in which a sulfurized vegetable based oil with no cross linker was added to the asphalt before addition of the polymer (Blend B).

[00076] Blend A is a modified asphalt binder comprising:

- 95.56% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 4.2% of refined soy bean oil by weight of the blend.
- 0.24% of Styrene-Butadiene Styrene (Kraton D-1192) by weight of the blend.
- 0.004% of elemental sulfur by weight of the blend.

[00077] Blend B is a modified asphalt binder comprising:

- 95.56% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.

- 4.2% of a sulfurized refined soy bean oil reacted with 7.0% by weight of elemental sulfur at 175°C for 33 hrs under a Nitrogen sparge. This resulted in a modifier with 70.0% oligomers. It will be hereby referred to as VSBO70.
- 0.24% of Styrene-Butadiene Styrene (Kraton D-1192) by weight of the blend.

Blending Procedure:

1. The oil was blended into the asphalt after the binder had been annealed at 150°C for 1 hour. The modified binder heated to about 193°C for polymer modification.
2. The RPM in the high shear mixer was set to 1000 while the SBS was added (within 1 minute). Immediately after addition of the polymer the RPM was briefly ramped up to 3000 rpm for approximately 10 minutes to insure full break down of the SBS pellets, after which the shear level was lowered to 1000 rpm.
3. Polymer blending was continued at 1000 rpm for a total of 2 hrs.
4. If a cross linker step is needed, the temperature was dropped to about 182°C at a 150 rpm at which point the sulfur cross linker was added. Blending was continued at 182°C and 150 rpm for 2 hrs.
5. Samples were taken from the Polymer modified binder before and after it was placed in an oven at 150°C for curing for approximately 12hrs (overnight) to achieve full swelling of the polymer.

[00078] Performance grade tests were performed in accordance to AASHTO M320. Multiple Stress Creep and Recovery tests were performed on the unaged binder at 34°C in accordance to AASHTO T350. Details are shown in Table 2:

Table 2

Binder Name	Blend Conditions				J_m at 34°C, 3.2 kPa	%Recovery at 34°C, 3.2 kPa
	Cross- linker Added	12hr Curing	Blend Time	SBS/Oil Ratio		
PG64-22 +4.2%SBO + 0.24%SBS + 0.02%S	Yes	No	4 hours	0.05	0.21	14.23
	Yes	Yes		0.05	0.17	17.40
PG64-22 +4.2%VSBO70 + 0.24%SBS	No	No	2 hour	0.05	0.15	16.18
	No	Yes		0.05	0.13	17.35

[00079] The results show that use of the sulfurized vegetable based oil eliminate the need for a cross-linker by delivering equal elasticity and performance at the conclusion of blending and curing, thus significantly simplifying the modification process for the end user. Furthermore, as a result of eliminating the crosslinking step the blend time was significantly reduced from 4 hrs to 2 hr.

Example 3: Use of sulfurized vegetable-based oil as polymer compatibilizer and cross-linker:

[00080] Two polymer modified asphalt blends were compared, one in which elemental sulfur was added directly to the asphalt to cross link the SBS following a conventional asphalt polymer modification procedure (Blend A), and the other in which a sulfurized vegetable based oil while no cross linker was added to the asphalt before the addition of the polymer (Blend B).

[00081] Blend A is a modified asphalt binder comprising:

- 95.56% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 4.2% of refined soy bean oil by weight of the blend.
- 0.24% of Styrene-Butadiene Styrene (Kraton D-1192) by weight of the blend.
- 0.004% of elemental sulfur by weight of the blend.

[00082] Blend B is a modified asphalt binder comprising:

- 95.56% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 4.2% of a polymerized vegetable-based oil (containing 0.0018% sulfur by weight of the asphalt), as described below:
 - 60% by weight of a sulfurized refined soy bean oil reacted with 7.0% by weight of elemental sulfur at 175°C for 33 hrs under a Nitrogen sparge. This resulted in a modifier with 70.0% oligomers. It will be hereby referred to as VSBO70.
 - 40% by weight of refined soy bean oil
 - Blend of VSBO70 and the unmodified oil had a 45% oligomer content. It will be hereby referred to as VSBO45.
- 0.24% of Styrene-Butadiene Styrene (Kraton D-1192) by weight of the blend.

Blending Procedure:

1. The oil was blended into the asphalt after the binder had been annealed at 150°C for 1 hour. The modified binder heated to about 193°C for polymer modification.

2. The RPM in the high shear mixer was set to 1000 while the SBS was added (within 1 minute). Immediately after addition of the polymer the RPM was briefly ramped up to 3000 rpm for approximately 10 minutes to insure full break down of the SBS pellets, after which the shear level was lowered to 1000 rpm.
3. Polymer blending was continued at 1000 rpm for a total of 2 hrs.
4. If a cross linker step is needed, the temperature was dropped to about 182°C at a 150 rpm at which point the sulfur cross linker was added. Blending was continued at 182°C and 150 rpm for 2 hrs.
5. Samples were taken from the Polymer modified binder before and after it was placed in an oven at 150°C for curing for approximately 12- hrs (overnight) to achieve full swelling of the polymer.

[00083] Performance grade tests were performed in accordance to AASHTO M320. Multiple Stress Creep and Recovery tests were performed on the unaged binder at 34°C in accordance to AASHTO T350. Details are shown in Table 3:

Table 3

Binder Name	Blend Conditions				J_{ir} at 34°C, 3.2 kPa	%Recovery at 34°C, 3.2 kPa
	Cross- linker Added	12hr Curing	Blend Time	SBS/Oil Ratio		
PG64-22 +4.2%SBO + 0.24%SBS + 0.02%S	Yes	No	4 hours	0.05	0.21	14.23
	Yes	Yes		0.05	0.17	17.40
PG64-22 +4.2%VSBO45 + 0.24%SBS	No	No	1 hour	0.05	0.16	15.76
	No	Yes		0.05	0.12	19.01

[00084] The results show that use of the sulfurized vegetable based oil eliminated the need for a cross-linker by delivering a superior elasticity and performance at the conclusion of blending. Furthermore, the total sulfur present in the sulfurized vegetable oil (of which only a fraction is reactive at the blend conditions) was less than half of the elemental sulfur crosslinker added to the asphalt in Blend A, thus highlighting the much higher efficiency in crosslinking achieved when the sulfurized oil is used as a replacement for use of elemental sulfur as a crosslinker.

[00085] The results also signify that the use of the sulfurized oil developed a more efficient and higher elasticity elastomeric polymer compared to the binder that did not contain the sulfurized modifier at the conclusion of the curing step. Furthermore, as a result of eliminating the crosslinking step the blend time was significantly reduced from 4 hrs to 1 hr.

Example 4: Use of Reacted Vegetable-based Thermoplastic Polymer based on Soybean Oil #1:

[00086] Two polymer modified asphalt blends were compared, one in which elemental sulfur was added directly to the asphalt to cross link the SBS following a conventional asphalt polymer modification procedure (Blend A), and the other in which a reacted SBS-vegetable based oil blend was used as a thermoplastic polymer replacement and the only additive (Blend B).

[00087] Blend A is a modified asphalt binder comprising:

- 95.56% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 4.2% of refined soy bean oil by weight of the blend.
- 0.24% of Styrene-Butadiene Styrene (Kraton D-1192) by weight of the blend.
- 0.004% of elemental sulfur by weight of the blend.

[00088] Blend B is a modified asphalt binder comprising:

- 95.56% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 4.44% of a reacted thermoplastic polymer blend (containing 0.0029% sulfur by weight of the asphalt), as described below:
 - 95% by weight of a sulfurized refined soy bean oil reacted with 7.0% by weight of elemental sulfur at 175°C for 33 hrs under a Nitrogen sparge. This resulted in a modifier with 70.0% oligomers (VSBO70).
 - 5% by weight of Styrene-Butadiene Styrene (Kraton D-1192)
 - The VSBO70 was heated to 195°C under light agitation at which point the D-1192 SBS was gradually added and continued to be reacted for 60 minutes after which the reacted blend was cooled.

Blending Procedure:

1. The oil was blended into the asphalt after the binder had been annealed at 150°C for 1 hour. The modified binder heated to about 193°C for polymer modification.
2. The RPM in the high shear mixer was set to 1000 while the SBS was added (within 1 minute). Immediately after addition of the polymer the RPM was briefly ramped up to 3000

rpm for approximately 10 minutes to insure full break down of the SBS pellets, after which the shear level was lowered to 1000 rpm.

3. Polymer blending was continued at 1000 rpm for a total of 2 hrs.
4. If a cross linker step is needed, the temperature was dropped to about 182°C at a 150 rpm at which point the sulfur cross linker was added. Blending was continued at 182°C and 150 rpm for 2 hrs.
5. Samples were taken from the Polymer modified binder before and after it was placed in an oven at 150°C for curing for approximately 12hrs (overnight) to achieve full swelling of the polymer.

[00089] Multiple Stress Creep and Recovery tests were performed on the unaged binder at 34°C in accordance to AASHTO T350. Details are shown in Table 4:

Table 4

Binder Name	Blend Conditions				J_m at 34°C, 3.2 kPa	%Recovery at 34°C, 3.2 kPa
	Cross- linker- Added	12hr Curing	Blend Time	SBS/Oil Ratio		
PG64-22 +4.2%SBO ÷ 0.24%SBS + 0.02%S	Yes	No	4 hours	0.05	0.21	14.23
	Yes	Yes		0.05	0.17	17.40
PG64-22 +4.44%(VSBO70-SBS 95:5)	No	No	1 hour	0.05	0.10	22.14
	No	Yes		0.05	0.09	23.38

[00090] The results show a significant increase in elasticity and creep stiffness (reduction in creep compliance) with the use of the reacted vegetable oil-SBS thermoplastic polymer in place of conventional SBS modification, even though the SBS content of the asphalt binders remained unchanged. Furthermore, use of the reacted vegetable oil-SBS thermoplastic polymer eliminated the need for addition of a cross-linker. This can significantly improve and simplify the modification process for the end user, as the use of three additives (oil, SBS, and sulfur) is reduced to a single step modification with enhanced performance that required less than half of the blend time of the conventional blends (1 hrs instead of 4 hrs).

Example 5: Use of Reacted Vegetable-based Thermoplastic Polymer based on Soybean Oil #2:

[00091] Two polymer modified asphalt blends were compared, one in which elemental sulfur was added directly to the asphalt to cross link the SBS following a conventional asphalt

polymer modification procedure (Blend A), and the other in which a reacted SBS-vegetable based oil blend was used as a thermoplastic polymer replacement and the only additive (Blend B).

[00092] Blend A is a modified asphalt binder comprising:

- 94.58% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 4.2% of refined soy bean oil by weight of the blend.
- 1.2% of Styrene-Butadiene Styrene (Kraton D-1192) by weight of the blend.
- 0.02% of elemental sulfur by weight of the blend.

[00093] Blend B is a modified asphalt binder comprising:

- 94.6% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 5.4% of a reacted thermoplastic polymer blend (containing 0.0018% sulfur by weight of the asphalt), as described below:
 - 78% by weight of a sulfurized refined soy bean oil reacted with 7.0% by weight of elemental sulfur at 175°C for 33 hrs under a Nitrogen sparge. This resulted in a modifier with 70.0% oligomers, blended back with refined SBO to a 45% oligomer content (VSBO45).
 - 22% by weight of Styrene-Butadiene Styrene (Kraton D-1192)
 - The VSBO45 was heated to 195°C under light agitation at which point the D-1192 SBS was gradually added and continued to be reacted for 60 minutes after which the reacted blend was cooled.

Blending Procedure:

1. The oil was blended into the asphalt after the binder had been annealed at 150°C for 1 hour (Blend A only). The modified binder heated to about 193°C for polymer modification.
2. The RPM in the high shear mixer was set to 1000 while the SBS was added (within 1 minute). Immediately after addition of the polymer the RPM was briefly ramped up to 3000 rpm for approximately 10 minutes to insure full break down of the SBS pellets, after which the shear level was lowered to 1000 rpm.
3. Polymer blending was continued at 1000 rpm for a total of 2 hrs.
4. If a cross linker step is needed, the temperature was dropped to about 182°C at a 150 rpm at which point the sulfur cross linker was added. Blending was continued at 182°C and 150 rpm for 2 hrs.

5. Samples were taken from the Polymer modified binder before and after it was placed in an oven at 150°C for curing for approximately 12 hrs (overnight) to achieve full swelling of the polymer.

[00094] Performance grade tests were performed in accordance to AASHTO M320. Multiple Stress Creep and Recovery tests were performed on the unaged binder at 34°C in accordance to AASHTO T350. Details are shown in Table 5:

Table 5

Binder Name	Blend Conditions				J_{sr} at 34°C, 3.2 kPa	%Recovery at 34°C, 3.2 kPa
	Cross- linker Added	12hr Curing	Blend Time	SBS/Oil Ratio		
PG64-22 +4.2%SBO + 1.2%SBS + 0.02%S	Yes	No	4 hours	0.22	0.128	28.97
	Yes	Yes		0.22	0.122	29.72
PG64-22 +5.4%(VSBO45-SBS 78:22)	No	No	1 hour	0.22	0.10	27.40
	No	Yes		0.22	0.08	32.81

[00095] The results show a significant increase in elasticity and creep stiffness (reduction compliance) with the use of the reacted vegetable oil-SBS thermoplastic polymer in place of conventional SBS modification, even though the SBS content of the asphalt binders remained unchanged. Furthermore, use of the reacted vegetable oil-SBS thermoplastic polymer eliminated the need for addition of a cross-linker. This can significantly improve and simplify the modification process for the end user, as the use of three additives (oil, SBS, and sulfur) is reduced to a single step modification with enhanced performance that only required less than half of the blend time of conventional blends.

Example 6: Comparison of Reacted Vegetable-based Thermoplastic Polymers:

[00096] Two polymer modified asphalt blends were compared in which unreacted and reacted SBS-vegetable based oil blend was used as a thermoplastic polymer replacement and the only additive (Blends A and B).

[00097] Blend A is a modified asphalt binder comprising:

- 94.0% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.

- 6% of a reacted thermoplastic polymer blend, as described below:
 - 70% by weight of RCO.
 - 30% by weight of Styrene-Butadiene Styrene (Kraton D-1192)
 - The RCO was heated to 195°C under light agitation at which point the D-1192 SBS was gradually added and continued to be agitated until a uniform blend was achieved (approximately 15-30 minutes). At this point the elemental sulfur was added at the equivalent of 1/60 of the SBS content for 60 minutes, after which the reacted blend was cooled.

[00098] Blend B is a modified asphalt binder comprising:

- 94.0% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 6% of a reacted thermoplastic polymer blend (containing 0.0018% sulfur by weight of the asphalt), as described below:
 - 70% by weight of a sulfurized refined soy bean oil reacted with 7.0% by weight of elemental sulfur at 175°C for 33 hrs under a Nitrogen sparge. This resulted in a modifier with 70.0% oligomers, blended back with refined SBO to a 45% oligomer content (VSBO45).
 - 30% by weight of Styrene-Butadiene Styrene (Kraton D-1192)
 - The VSBO45 was heated to 195°C under light agitation at which point the D-1192 SBS was gradually added and continued to be reacted for 60 minutes after which the reacted blend was cooled.

Blending Procedure:

1. The oil was blended into the asphalt after the binder had been annealed at 150°C for 1 hour (Blend A only). The modified binder heated to about 193°C for polymer modification.
2. The RPM in the high shear mixer was set to 1000 while the SBS was added (within 1 minute). Immediately after addition of the polymer the RPM was briefly ramped up to 3000 rpm for approximately 10 minutes to insure full break down of the SBS pellets, after which the shear level was lowered to 1000 rpm.
3. Polymer blending was continued at 1000 rpm for a total of 2 hrs.
4. If a cross linker step is needed (Blends A and B), the temperature was dropped to about 182°C at a 150 rpm at which point the sulfur cross linker was added. Blending was continued at 182°C and 150 rpm for 2 hrs.

5. Samples were taken from the Polymer modified binder before and after it was placed in an oven at 150°C for curing for approximately 12 hrs (overnight) to achieve full swelling of the polymer.

Multiple Stress Creep and Recovery tests were performed on the unaged binder at 34°C in accordance to AASHTO T350. Details are shown in

[00099] Table 6:

Table 6

Binder Name	Blend Conditions				J_m at 34°C, 3.2 kPa	%Recovery at 34°C, 3.2 kPa
	Cross- linker Added	12hr Curing	Blend Time	SBS/Oil Ratio		
PG64-22 +6.0%(RCO-SBS 70:30)	No	No	2 hours	0.30	0.13	27.70
PG64-22 +6.0%(VSBO45-SBS 70:30)	No	No	1 hour	0.30	0.08	35.26
	No	Yes		0.30	0.07	39.33

[000100] The results show a difference between the thermoplastic polymer-oil blend in which the sulfur was added separately to the asphalt blend, and the reacted thermoplastic polymer blend based on the use of a sulfurized vegetable oil. The unreacted thermoplastic blend did not achieve the same elasticity and performance of that of the reacted blend, and the later addition of the corsslinker into the bitumen did not overcome this difference in performance. It should be noted that the source of the biorenewable oil was also different between Blend A and B, the effect of which cannot be dismissed. However, the general trend of the results highlight the preference of the use of the reactive sulfur in the sulfurized vegetable based oil as the preferred method of attaining a reacted thermoplastic polymer and biorenewable oil blend.

[000101] A significant increase in elasticity and creep stiffness (reduction in creep compliance) was observed with the use of the reacted vegetable oil-SBS thermoplastic polymer in place of conventional SBS modification, even though the SBS content of the asphalt binders remained unchanged. Furthermore, use of the reacted vegetable oil-SBS thermoplastic polymer eliminated the need for adding a separate cross linker. This can significantly improve and simplify the modification process for the end user, as the use of three additives (oil, SBS, and sulfur) is reduced to a single step modification with enhanced performance that only required less than half of the blend time of conventional blends.

Example 7: Comparison of Blending Conditions for Unreacted Vegetable-based Thermoplastic Polymers:

[000102] Three polymer modified asphalt blends were compared in which unreacted SBS-vegetable based oil was used as a thermoplastic polymer replacement and the only additive. Blend conditions were varied in the Blends A, B, and C in terms of shearing and blending temperature as well as addition of a cross linker.

[000103] Blend A is a modified asphalt binder that was manually homogenized at 175°C for 1 minute, comprising:

- 94.0% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 6% of a reacted thermoplastic polymer blend, as described below:
 - 50% by weight of RCO.
 - 50% by weight of Styrene-Butadiene Styrene (Kraton D-1192)
 - The RCO was heated to 195°C under light agitation at which point the D-1192 SBS was gradually added and continued for 2 hrs

[000104] Blend B is a modified asphalt binder that was high shear blended at 193°C for 2 hrs, comprising:

- 94.0% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 6% of a reacted thermoplastic polymer, as described below:
 - 50% by weight of RCO.
 - 50% by weight of Styrene-Butadiene Styrene (Kraton D-1192)
 - The RCO was heated to 195°C under light agitation at which point the D-1192 SBS was gradually added and continued for 2 hrs

[000105] Blend C is a modified asphalt binder that was high shear blended at 193°C for 2 hrs, comprising:

- 93.95% neat asphalt binder graded as PG64-22 (PG 65.7-24.9) by weight of the blend.
- 6% of a reacted thermoplastic polymer, as described below:
 - 50% by weight of RCO.
 - 50% by weight of Styrene-Butadiene Styrene (Kraton D-1192)
 - The RCO was heated to 195°C under light agitation at which point the D-1192 SBS was gradually added and continued for 2 hrs
- 0.05% by weight of elemental sulfur added as a cross-linker.

Multiple Stress Creep and Recovery tests were performed on the unaged binder at 34°C in accordance to AASHTO T350. Details are shown in

[000106] Table 7:

Table 7

Binder Name	Blend Conditions				J_{re} at 34°C, 3.2 kPa	%Recovery at 34°C, 3.2 kPa
	Cross- linker Added	12hr Curing	Blend Time	SBS/Oil Ratio		
PG64-22 +6.0%(RCO-SBS 50:50) – Hand Blended at 175°C	<u>No</u>	No	2 hours	0.50	0.10	29.45
PG64-22 +6.0%(RCO-SBS 50:50) – High Shear Blended	<u>No</u>	No	2 hours	0.50	0.08	32.88
PG64-22 +6.0%(RCO-SBS 50:50) + 0.05%S - High Shear Blended	<u>Yes</u>	Yes	2 hours	0.50	0.05	49.12

[000107] The results highlight a few important aspects of the invention:

- It was possible to get partial performance from the thermoplastic polymer by blending at 175°C at very low shear levels. With conventional SBS modification, it is often not possible to get polymer elasticity at temperatures lower than approximately 185°C and without high shear blending to initially break down the polymer.
- The unreacted thermoplastic polymer blend (Blend C) did not exhibit the full performance exhibited by the conventional polymer modification.
- Addition of sulfur to the asphalt blend containing the unreacted thermoplastic polymer significantly enhanced the performance beyond that of the conventional modification without a cross-linker.
- It is noted as a reminder that example 6 showed that sulfur reaction through the use of the active sulfur in the sulfurized vegetable oils resulted in the highest performing thermoplastic polymer.

Example 8: Modified Vegetable Oil Based Thermoplastic Elastomeric Polymer (MVOTPP)

[000108] A modified asphalt binder comprising:

- 96.5% by weight of neat asphalt binder graded as PG58-28 (PG 62.1-29.9)
- 4.5% by weight of a blend comprising:

- 78% by weight of a functionalized Polyolefin (Titan 7686).
- 22% by weight of Cobalt Catalyzed (500 ppm) Blown Recovered Corn Oil, reacted at 115°C for 9 hrs and having a 24% oligomer content.
- The polymerized oil was heated to 130°C under light agitation at which point the oxidized polyethylene was gradually added. The reaction was continued for 1 hr. The end product (referred to hereby as MVOTPP) was a soft brittle solid that was easily flaked. Figure 9 shows the thermal analysis results for the end product.

The modifier was blended into the asphalt after the binder had been annealed at 150°C for 1 hour. Performance grade tests were performed in accordance to AASHTO M320. The modification resulted in a 4.7°C low temperature grade improvement. The net change in the high and low performance grade resulted in a very significant 1.9°C improvement in the Useful Temperature Interval. Details are shown in

[000109] Table 8:

Table 8

Binder Name	UTI	O-DSR	R-DSR	S-BBR	m-BBR
	°C	°C	°C	°C	°C
Unmodified	92.0	62.14	62.88	-29.9	-29.9
+4.5% MVOTPP	93.8	59.18	59.53	-34.6	-36.9

[000110] The thermoplastic plastomeric polymer based on the incorporation of the blown recovered corn oil modifier achieved one low temperature grade improvement while still passing the PG58 high temperature grade specification. This is a significant achievement, as end users will almost exclusively need to use two modifiers to achieve the low temperature grade improvement while maintaining the base high temperature grade.

Example 9: Modified Vegetable Oil Based Thermoplastic Plastomeric Polymer (MVOTPP#1)

[000111] The thermoplastic polymer described in Example 8 (MVOTPP#1) was compared to the unmodified neat asphalt and asphalt only modified with the Titan 7686 Oxidized Polyethylene.

- The dosage of the MVOTPP#1 was 4.5% by weight of the modified asphalt.
- The dosage of the functionalized polyolefin (Titan 7686) was 1% (equivalent to the dosage used in the MVOTPP#1, based on the reaction charges).

[000112] Using a dynamic shear rheometer a step-wise temperature sweep was performed on each of the described binders. A concentric cylinder geometry was used to facilitate accurate

measurements at high temperatures and low viscosities. The temperature was ramped up between 15 and 150°C. At 5°C increments a 10 minute equilibration time step was defined, followed by loading at 1 Hz at a 1% strain amplitude from which the complex modulus was derived over the range of temperature steps. The results are shown in Figure 10.

[000113] The results shown in Figure 10 highlight an important aspect of the MVOTPP, namely the ideal effect on the base asphalt modulus across the temperature range of interest in asphalt applications:

- At temperatures between 100 and 150°C, the MVOTPP#1 reduced the complex modulus and dynamic viscosity by an average of 28%. This translates to high potential for enhancing workability and compaction. Thus the MVOTPP#1 offers the benefits of a “Compaction Aid Additive” at this temperature range.
- At temperatures between 40 and 100°C, the MVOTPP#1 increased the complex modulus and dynamic viscosity by an average of 115%. Thus the MVOTPP#1 behaves as a high temperature performance grade modifier at this temperature range.
- At temperatures lower than 40°C the MVOTPP#1 reduced the complex modulus and dynamic viscosity by an average of 37% (down to the 15°C measured during this test). Thus the MVOTPP#1 offers the benefit of a low temperature modifier at this temperature range.

Example 10: Modified Vegetable Oil Based Thermoplastic Plastomeric Polymer (MVOTPP#2)

[000114] A triaminononane (TAN) stearamide was produced as a thermoplastic polymeric wax as follows: Charges were calculated so that the reaction product will achieve the desired amine and acid value (Acid value of 0-5 mg KOH/g and amine value of 0-30 mg KOH/g). The fatty material, in this case a hydrogenated distillate from the vegetable refining process, was melted in an oven and charged at a 306.43g to a 1-L flask and a condenser was setup to condense any water and fatty distillate carried over as well as water from the reaction. The fatty acid was heated to 100°C under a nitrogen sparge. Once the flask reached target temperature, TAN (58.36g) was added slowly via an addition funnel over a half hour to control the resulting exothermic reaction. The reaction was then heated to between 160°C and allowed to react until the acid value leveled within the desired range, indicating the level of fatty acid containing

material consumption. The result was a thermoplastic polymer with a melting point of approximately 118°C.

[000115] A thermoplastic polymer was added at a 3% dosage to a PG64-22 binder. Using a dynamic shear rheometer a step-wise temperature sweep was performed on each of the described binders. A concentric cylinder geometry was used to facilitate accurate measurements at high temperatures and low viscosities. The temperature was ramped up between 15 and 150°C. At 5°C increments a 10 minute equilibration time step was defined, followed by loading at 1 Hz at a 1% strain amplitude from which the complex modulus was derived over the range of temperature steps. The results are shown in Figures 11 and 12.

Example 11: Modified Vegetable Oil Based Thermoplastic Plastomeric Polymer (MVOTPP#3)

[000116] An ethylene bis-stearamide (EBS) was produced as a thermoplastic polymeric wax as follows: Charges were calculated so that the reaction product will achieve the desired amine and acid value (Acid value of 0-5 mg KOH/g and amine value of 0-30 mg KOH/g). The fatty material, in this case a hydrogenated distillate from the vegetable refining process, was melted in an oven and charged at a 402.7 to a 1-L flask and a condenser was setup to condense any water and fatty distillate carried over as well as water from the reaction. The fatty acid was heated to 100°C under a nitrogen sparge. Once the flask reached target temperature, Ethylene Diamine (47.3g) was added slowly via an addition funnel over a half hour to control the resulting exothermic reaction. The reaction was then heated to between 170°C and allowed to react until the acid value leveled within the desired range, indicating the level of fatty acid containing material consumption.

[000117] The thermoplastic polymer was added at a 3% dosage to a PG64-22 binder. The thermoplastic polymer was produced as described below:

- 50% by weight of an Ethylene Bis-stearamide (EBS).
- 50% by weight of a refined soybean oil.
- The oil was heated to 130°C under light agitation at which point the EBS was gradually added. The reaction was continued for 1 hr. The end product (referred to herby as MVOTPP#3) was a soft brittle solid that was easily flaked.

[000118] Using a dynamic shear rheometer a step-wise temperature sweep was performed on each of the described binders. A concentric cylinder geometry was used to facilitate accurate measurements at high temperatures and low viscosities. The temperature was ramped up between 15 and 150°C. At 5°C increments a 10 minute equilibration time step was defined,

followed by loading at 1 Hz at a 1% strain amplitude from which the complex viscosity was derived over the range of temperature steps. The results are shown in Figure 13.

CLAIMS

1. A polymeric composition, comprising a random copolymer comprising three or more distinct monomers, wherein a first monomer is a biorenewable oil and a second monomer is a thermoplastic polymer.
2. The polymeric composition of claim 1, wherein the biorenewable oil has been cationically polymerized using Bronsted acids and Lewis acids.
3. The polymeric composition of claim 1, wherein the biorenewable oil has been polymerized using oxidation, super acid catalysis, bodying, or sulfurization techniques, or a combination thereof.
4. The polymeric composition of claim 1, wherein the copolymer is hyperbranched.
5. The polymeric composition of claim 1, wherein at least one monomer is sulfur.
6. The polymeric composition of claim 1, wherein at least one monomer is a vinylaromatic compound.
7. The polymeric composition of claim 1, wherein at least one monomer is styrene, butadiene, indene, divinylbenzene, or an alpha-olefin.
8. The polymeric composition of claim 1, for use in asphalt applications such as compaction aid additives, rheology modifiers for enhanced high and low temperature asphalt performance, rheology modifier with enhanced storage stability, rheology modifier with enhanced oxidative aging stability, compaction aid additive rheology modifier for enhanced low temperature performance while minimizing reduction in modulus at high temperature performance ranges, rejuvenator agent, recycling agent, and any combination thereof.
9. The polymeric composition of claim 1, for use in hot mix, warm mix, and cold mix asphalt applications, roofing asphalt, and coatings.
10. A polymeric composition, comprising a biorenewable oil and a thermoplastic polymer, wherein the thermoplastic polymer comprises about 1-75 wt% of the polymeric composition with a remaining balance of a biorenewable oil.
11. The polymeric composition of claim 10, wherein the thermoplastic polymer is an elastomer, a plastomer, a pre-polymer, an oligomer, or a high molecular weight polymer.
12. The polymeric composition of claim 10, wherein the thermoplastic polymer is a polyolefin.
13. The polymeric composition of claim 10, wherein the thermoplastic polymer is ground tire rubber.

14. The polymeric composition of claim 10, wherein the thermoplastic polymer is a styrene based copolymer.
15. The polymeric composition of claim 14, wherein the styrene based copolymer is a styrene-butadiene block copolymer.
16. The polymeric composition of claim 10, wherein the biorenewable oil is a plant-based, animal-based, or microbial-based oil.
17. The polymeric composition of claim 10, wherein the biorenewable oil is recovered corn oil or soybean oil.
18. The polymeric composition of claim 10, wherein the biorenewable oil is partially or fully hydrogenated oils, oils with conjugated bonds, or bodied oils wherein a heteroatom is not introduced.
19. The polymeric composition of claim 10, wherein the biorenewable oil is a previously modified, polymerized, or functionalized oil.
20. The polymeric composition of claim 10, wherein the biorenewable oil is at least partially sulfurized.
21. The polymeric composition of claim 10, further comprising a cross-linking agent.
22. The polymeric composition of claim 21, wherein the cross-linking agent is a sulfur containing compound or a peroxide.
23. The polymeric composition of claim 21, wherein the cross-linking agent is a sulfur containing compound and a compound selected from the group consisting of peroxide, polyphosphoric acid, and super acid catalysts.
24. The polymeric composition of claim 10, wherein the biorenewable oil is cationically polymerized.
25. The polymeric composition of claim 10, wherein the biorenewable oil is polymerized through oxidation, super acid catalysis, bodying, or sulfurization, or a combination thereof.
26. The polymeric composition of claim 10, for use in asphalt applications such as compaction aid additives, rheology modifiers for enhanced high and low temperature asphalt performance, rheology modifier with enhanced storage stability, rheology modifier with enhanced oxidative aging stability, compaction aid additive rheology modifier for enhanced low temperature performance while minimizing reduction in modulus at high temperature performance ranges, rejuvenator agent, recycling agent, and any combination thereof.

27. The polymeric composition of claim 10, for use in hot mix, warm mix, and cold mix asphalt applications, roofing asphalt, and coatings.
28. A modified asphalt, comprising:
 - an asphalt binder in an amount ranging from about 60-99.9 wt%;
 - an asphalt modifier in an amount ranging from about 0.1-40 wt%; wherein the asphalt modifier comprises:
 - about 1-75 wt% of a thermoplastic polymer and a remaining balance of biorenewable oil.
29. The modified asphalt of claim 28, wherein the thermoplastic polymer is a polyolefin.
30. The modified asphalt of claim 28, wherein the thermoplastic polymer is a styrene based copolymer.
31. The modified asphalt of claim 30, wherein the styrene based copolymer is a styrene-butadiene block copolymer.
32. The modified asphalt of claim 28, wherein the biorenewable oil is a plant-based, animal-based, or microbial-based oil.
33. The modified asphalt of claim 28, wherein the biorenewable oil is recovered corn oil or soybean oil.
34. The modified asphalt of claim 28, wherein the biorenewable oil is partially or fully hydrogenated oils, oils with conjugated bonds, or bodied oils wherein a heteroatom is not introduced.
35. The modified asphalt of claim 28, wherein the biorenewable oil is a previously modified, polymerized, or functionalized oil.
36. The modified asphalt of claim 28, wherein the biorenewable oil is at least partially sulfurized.
37. The modified asphalt of claim 28, wherein the asphalt modifier further comprises a cross-linking agent.
38. The modified asphalt of claim 37, wherein the cross-linking agent is a sulfur containing compound or a peroxide.
39. The modified asphalt of claim 37, wherein the cross-linking agent is a sulfur containing compound and a compound selected from the group consisting of peroxide, polyphosphoric acid, and super acid catalysts.
40. The modified asphalt of claim 28, wherein the biorenewable oil is cationically polymerized.

41. The modified asphalt of claim 28, wherein the biorenewable oil is polymerized through oxidation, super acid catalysis, bodying, or sulfurization, or a combination thereof.
42. A method of making a modified asphalt, comprising:
 - a. manufacturing an asphalt modifier, comprising:
 - i. heating a vulcanized biorenewable oil to a temperature exceeding that of the thermoplastic polymer's melting point;
 - ii. adding the thermoplastic polymer to the biorenewable oil and
 - iii. agitating the thermoplastic polymer with the biorenewable oil to obtain a homogeneous blend ;
 - b. blending the asphalt modifier into an asphalt binder.
43. The method of claim 42, wherein the modified asphalt comprises 0.1-40 wt% of the asphalt modifier and 60-99.9 wt% of the asphalt binder.
44. The method of claim 43, wherein a crosslinker agent is not required to deliver equal or better elasticity of conventional asphalt polymer modification procedures.
45. The method of claim 42, wherein step (b) takes at least 30% less blending time than conventional asphalt polymer modification procedures and delivers equal or better elasticity.
46. The method of claim 42, wherein step (b) takes at least 40% less blending time than conventional asphalt polymer modification procedures and delivers equal or better elasticity.
47. The method of claim 42, wherein step (b) takes at least 50% less blending time than conventional asphalt polymer modification procedures and delivers equal or better elasticity.
48. The method of claim 42, wherein step (b) takes at least 60% less blending time than conventional asphalt polymer modification procedures and delivers equal or better elasticity.
49. The method of claim 42, wherein the temperature during step (b) is at least 5°C below temperatures used in conventional asphalt polymer modification procedures.
50. The method of claim 42, wherein the temperature during step (b) is at least 10°C below temperatures used in conventional asphalt polymer modification procedures.
51. The method of claim 42, wherein the temperature during step (b) is at least 15°C below temperatures used in conventional asphalt polymer modification procedures.

52. The method of claim 42, wherein the temperature during step (b) is at least 20°C below temperatures used in conventional asphalt polymer modification procedures.
53. The method of claim 42, wherein the temperature during step (b) is at least 50°C below temperatures used in conventional asphalt polymer modification procedures.
54. The method of claim 42, wherein an additional curing step after step (b) is not required.
55. The method of claim 42, further comprising curing the asphalt modifier after step (b).
56. The method of claim 55, wherein the curing time is reduced by at least 60% compared to conventional asphalt polymer modification procedures.
57. The method of claim 55, wherein the curing time is reduced by at least 70% compared to conventional asphalt polymer modification procedures.
58. The method of claim 55, wherein the curing time is reduced by at least 80% compared to conventional asphalt polymer modification procedures.
59. A method of making a modified asphalt, comprising simultaneously blending a biorenewable oil and a thermoplastic polymer into an asphalt binder, wherein the biorenewable oil and the thermoplastic polymer together are an asphalt modifier.
60. The method of claim 59, wherein the modified asphalt comprises 0.1-40 wt% of the asphalt modifier and 60-99.9 wt% of the asphalt binder.
61. The method of claim 59, wherein the blending takes at least 30% less blending time than conventional asphalt polymer modification procedures and delivers equal or better elasticity.
62. The method of claim 59, wherein the blending takes at least 40% less blending time than conventional asphalt polymer modification procedures and delivers equal or better elasticity.
63. The method of claim 59, wherein the blending takes at least 50% less blending time than conventional asphalt polymer modification procedures and delivers equal or better elasticity.
64. The method of claim 59, wherein the temperature during blending is at least 5°C below temperatures used in conventional asphalt polymer modification procedures.
65. The method of claim 59, wherein the temperature during blending is at least 10°C below temperatures used in conventional asphalt polymer modification procedures.
66. The method of claim 59, wherein the temperature during blending is at least 15°C below temperatures used in conventional asphalt polymer modification procedures.

67. The method of claim 59, wherein the temperature during blending is at least 20°C below temperatures used in conventional asphalt polymer modification procedures.
68. The method of claim 59, wherein the temperature during blending is at least 50°C below temperatures used in conventional asphalt polymer modification procedures.
69. The method of claim 59, wherein an additional curing step after blending is not required.
70. The method of claim 59, further comprising curing the asphalt modifier after blending.
71. The method of claim 70, wherein the curing time is reduced by at least 60% compared to conventional asphalt polymer modification procedures.
72. The method of claim 70, wherein the curing time is reduced by at least 70% compared to conventional asphalt polymer modification procedures.
73. The method of claim 70, wherein the curing time is reduced by at least 80% compared to conventional asphalt polymer modification procedures.
74. The method of claim 59, further comprising adding a crosslinking agent to the asphalt binder.
75. The method of claim 74, wherein the crosslinking agent is a sulfur-containing compound.
76. The method of claim 74, wherein less than half of the amount of crosslinking agent is used compared to conventional asphalt polymer modification procedures.
77. A method of making a modified asphalt, comprising simultaneously blending a vulcanized biorenewable oil and a thermoplastic polymer into an asphalt binder, wherein the vulcanized biorenewable oil and the thermoplastic polymer together are an asphalt modifier.
78. The method of claim 77, wherein the asphalt modifier comprises 3 or more distinct monomers.
79. The method of claim 77, wherein the modified asphalt comprises 0.1-40 wt% of the asphalt modifier and 60-99.9 wt% of the asphalt binder.
80. The method of claim 77, wherein the blending takes at least 30% less blending time than conventional asphalt polymer modification procedures and delivers equal or better elasticity.
81. The method of claim 77, wherein the blending takes at least 40% less blending time than conventional asphalt polymer modification procedures and delivers equal or better elasticity.

82. The method of claim 77, wherein the blending takes at least 50% less blending time than conventional asphalt polymer modification procedures and delivers equal or better elasticity.
83. The method of claim 77 wherein the temperature during blending is at least 5°C below temperatures used in conventional asphalt polymer modification procedures.
84. The method of claim 77, wherein the temperature during blending is at least 10°C below temperatures used in conventional asphalt polymer modification procedures.
85. The method of claim 77, wherein the temperature during blending is at least 15°C below temperatures used in conventional asphalt polymer modification procedures.
86. The method of claim 77, wherein the temperature during blending is at least 20°C below temperatures used in conventional asphalt polymer modification procedures.
87. The method of claim 77, wherein the temperature during blending is at least 50°C below temperatures used in conventional asphalt polymer modification procedures.
88. The method of claim 77, wherein an additional curing step after blending is not required.
89. The method of claim 77, further comprising curing the asphalt modifier after blending.
90. The method of claim 89, wherein the curing time is reduced by at least 60% compared to conventional asphalt polymer modification procedures.
91. The method of claim 89, wherein the curing time is reduced by at least 70% compared to conventional asphalt polymer modification procedures.
92. The method of claim 89, wherein the curing time is reduced by at least 80% compared to conventional asphalt polymer modification procedures.

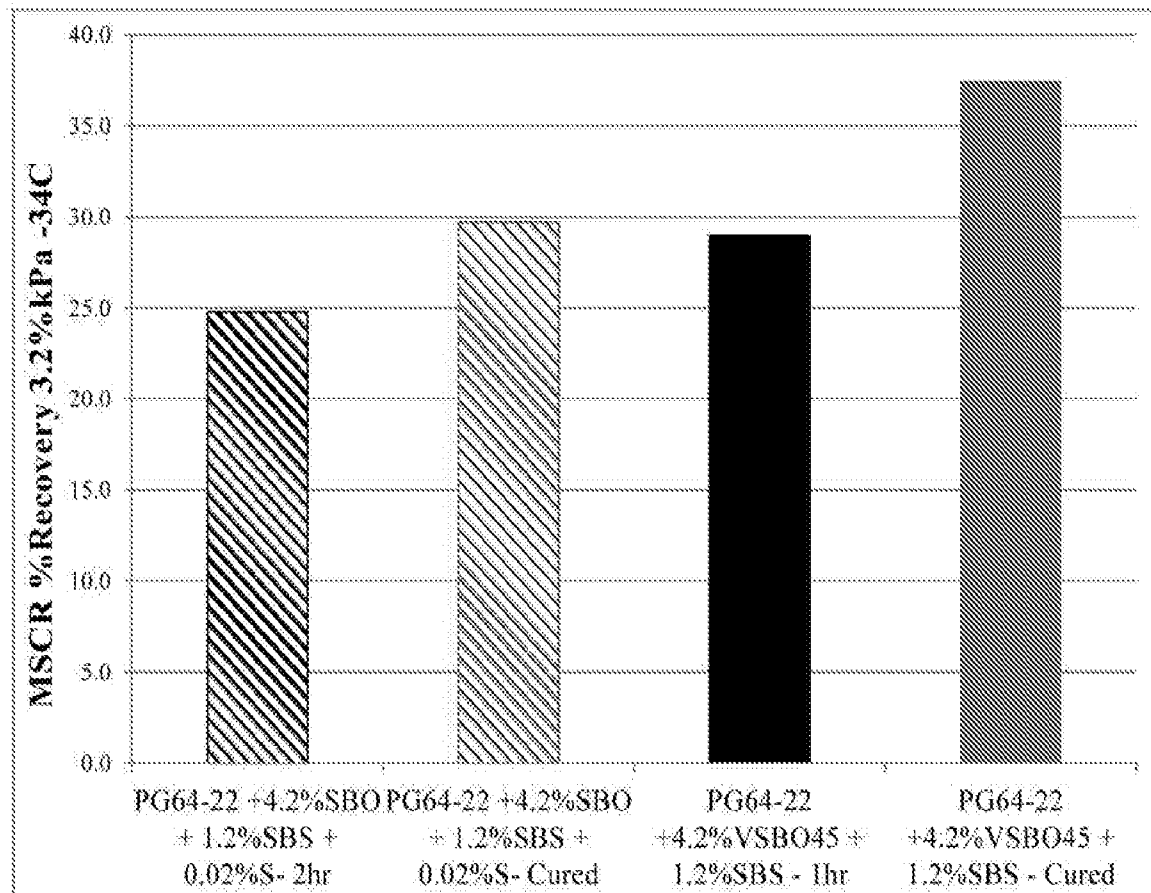


Figure 1

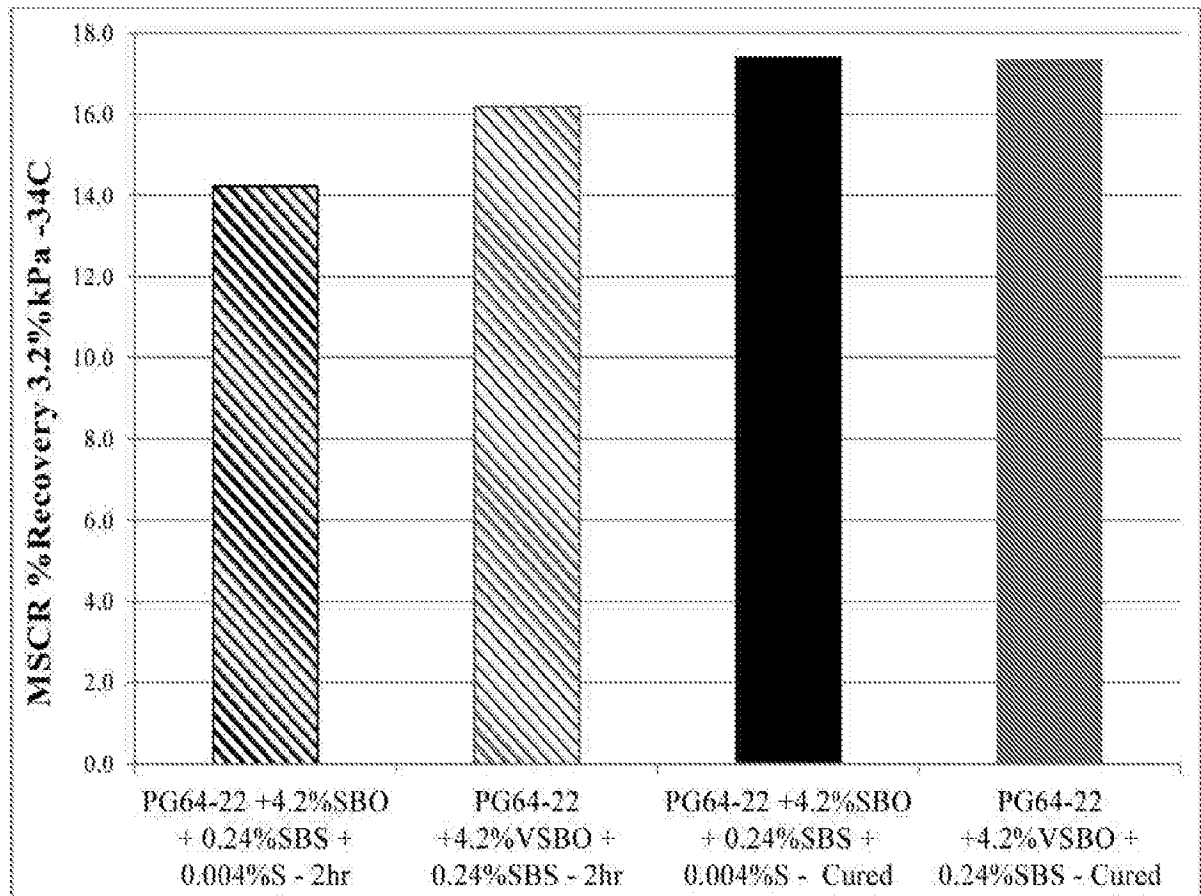


Figure 2

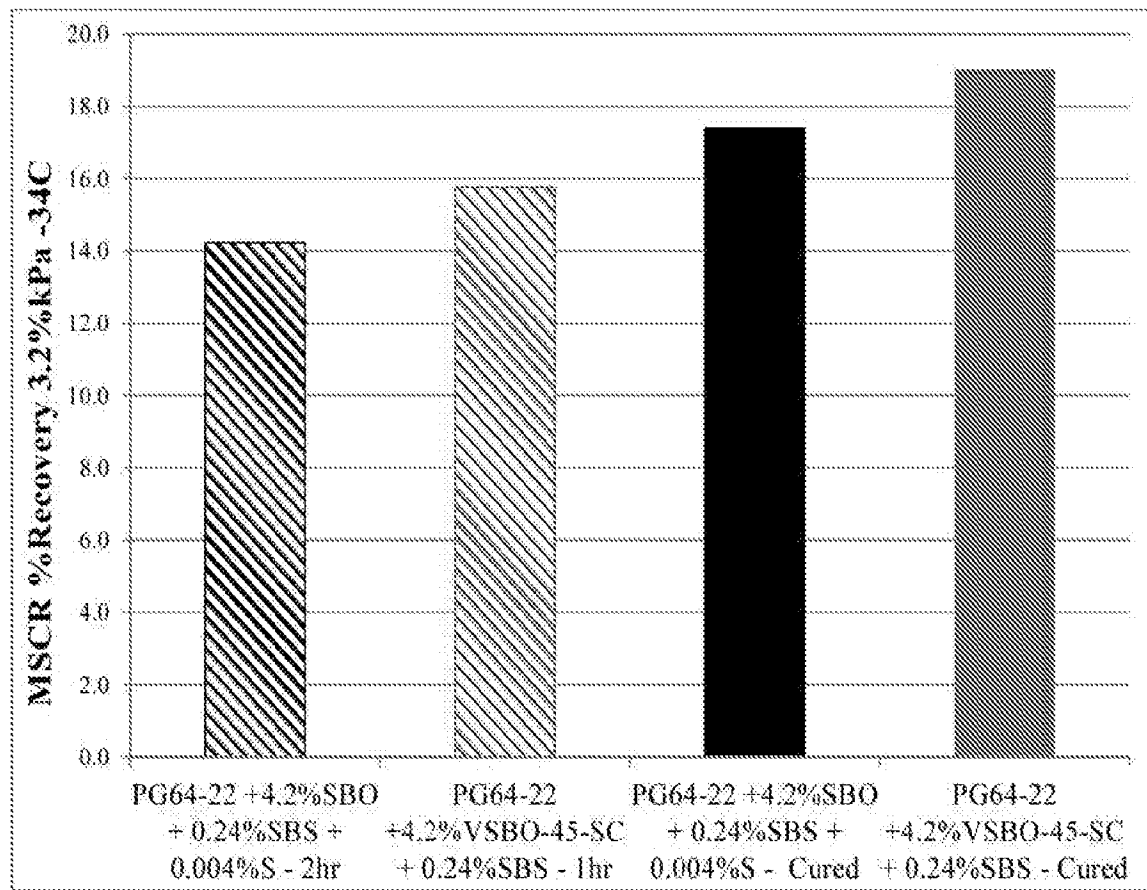


Figure 3

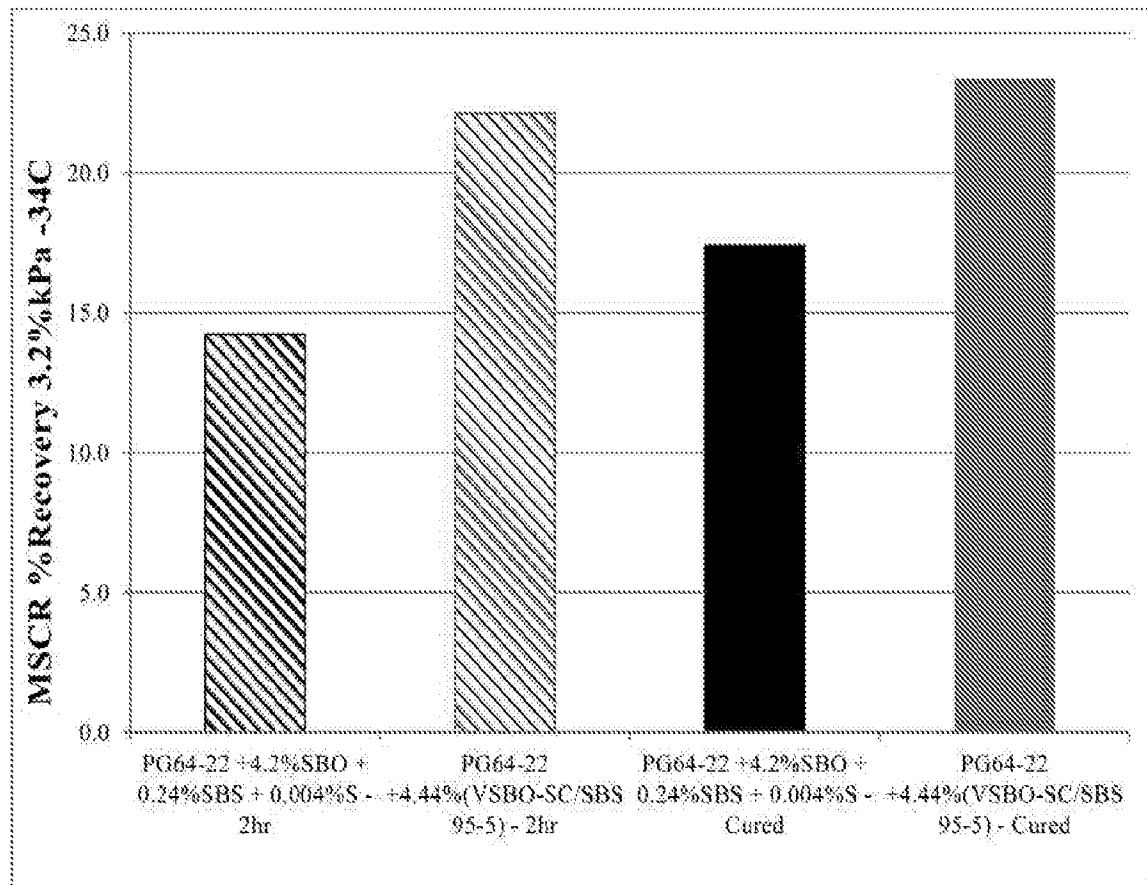


Figure 4

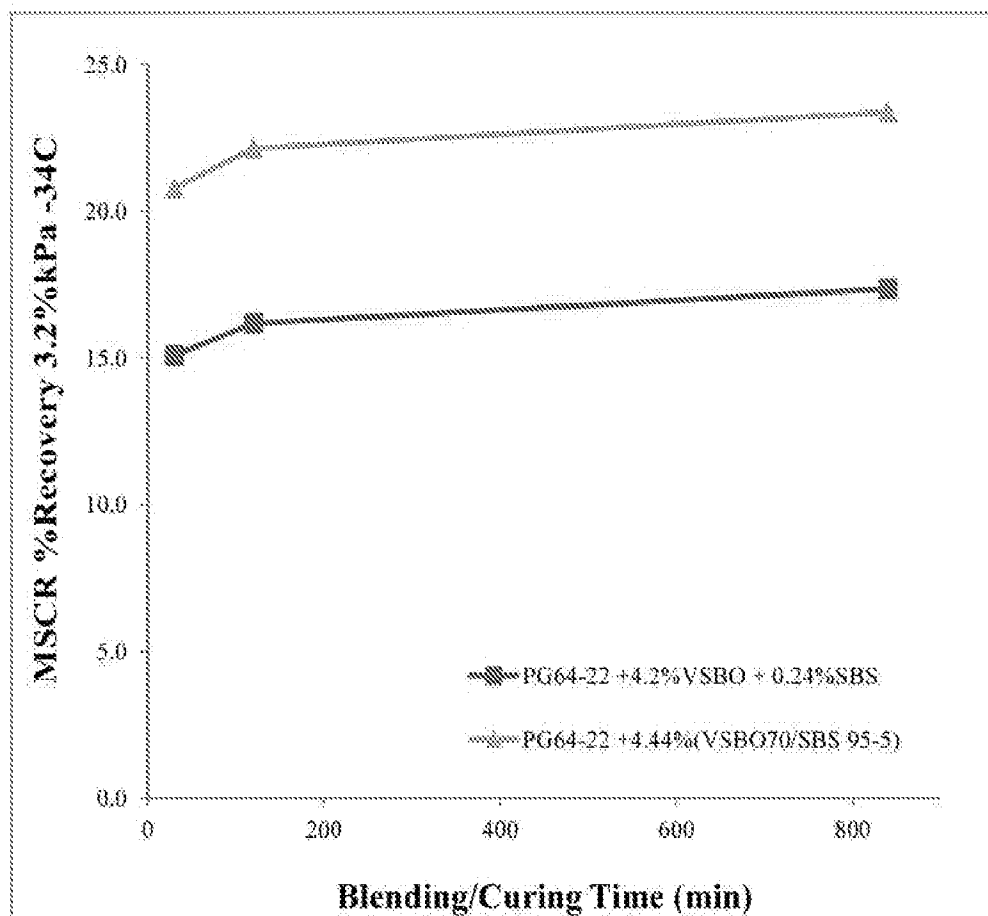


Figure 5

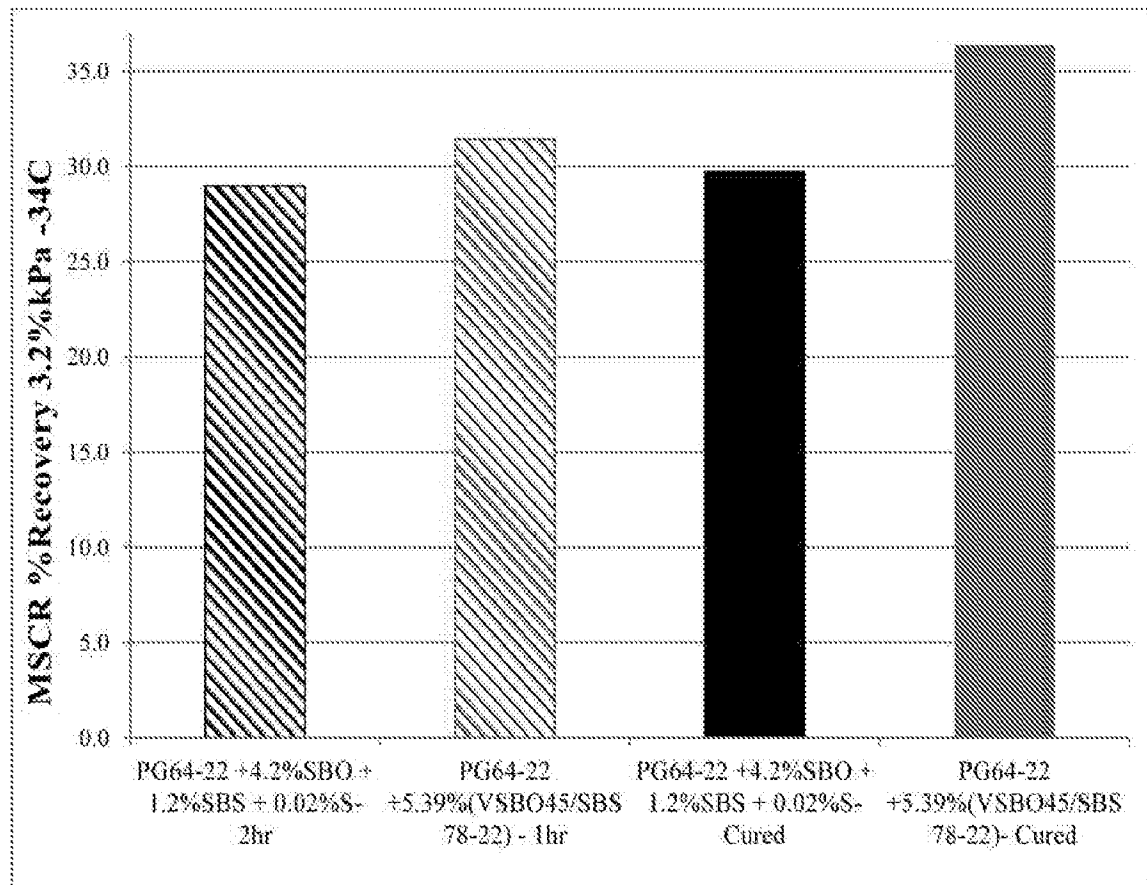


Figure 6

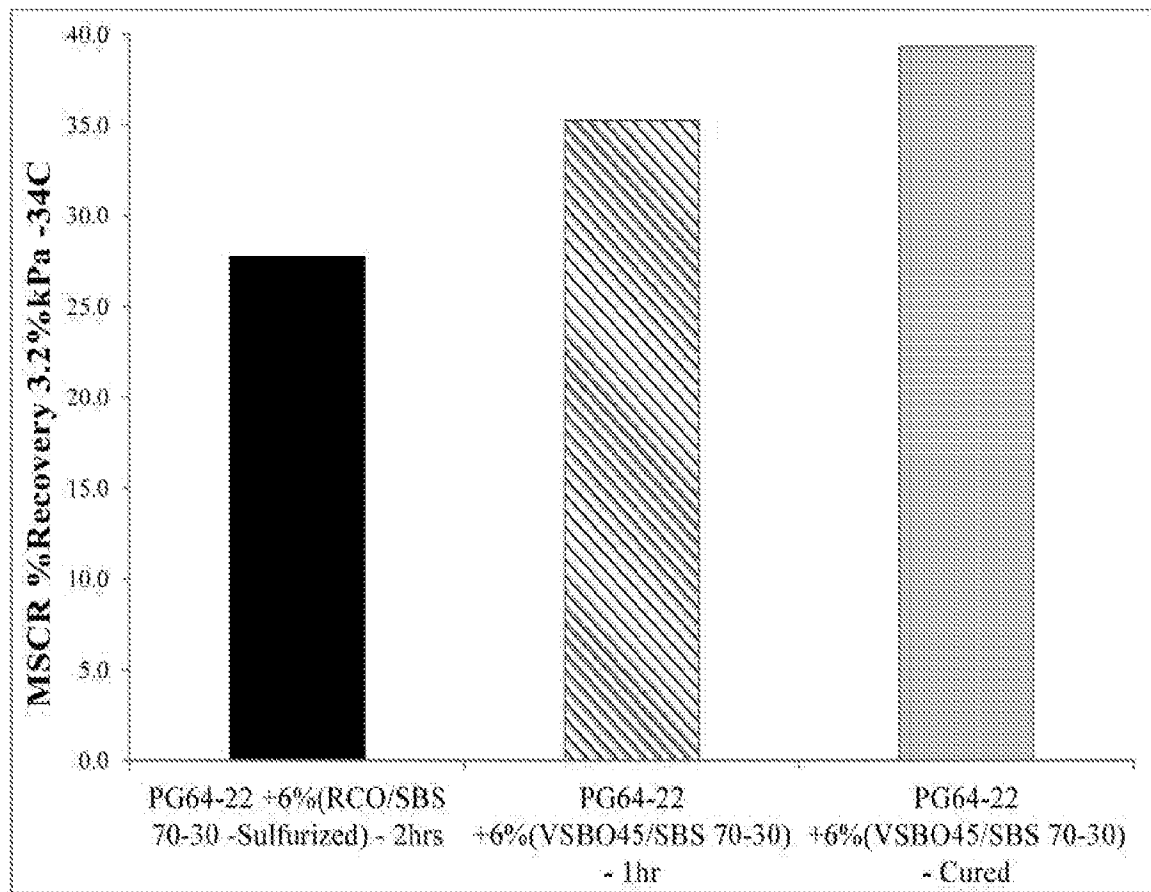


Figure 7

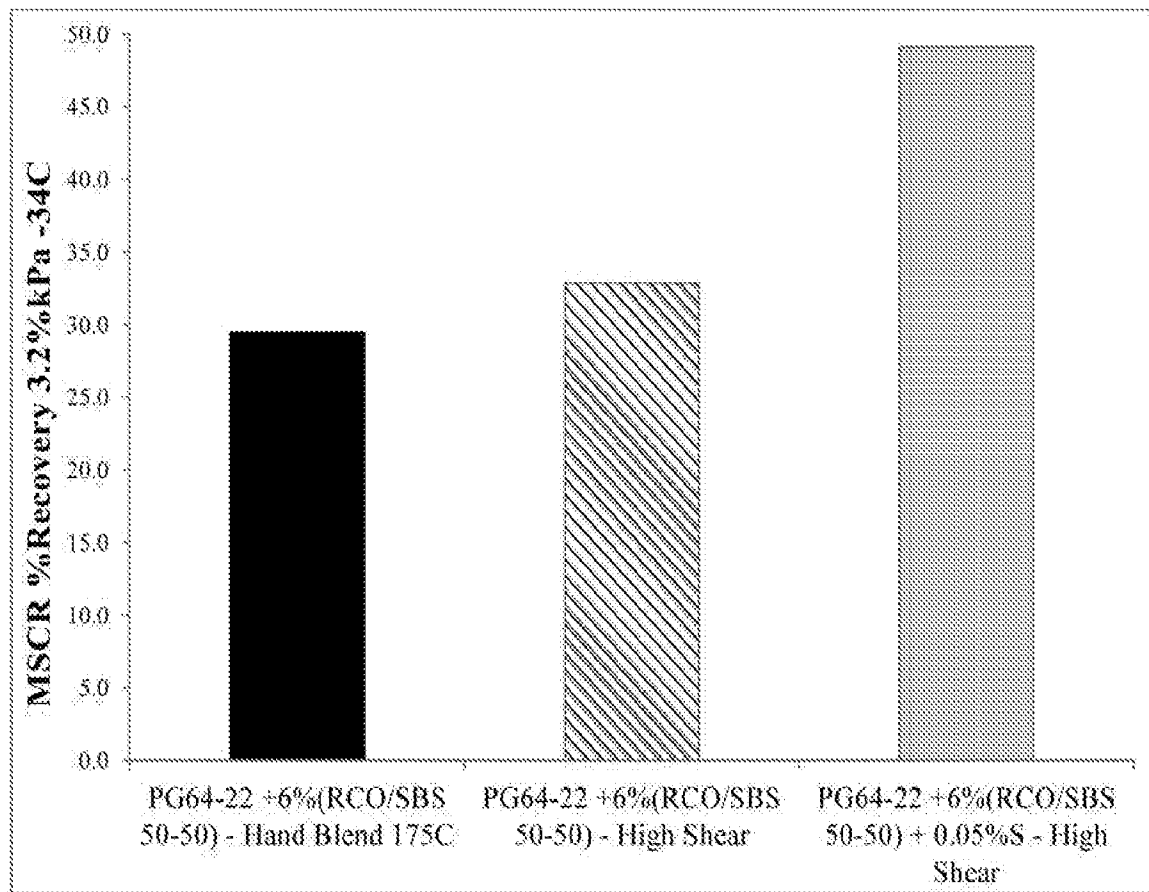


Figure 8

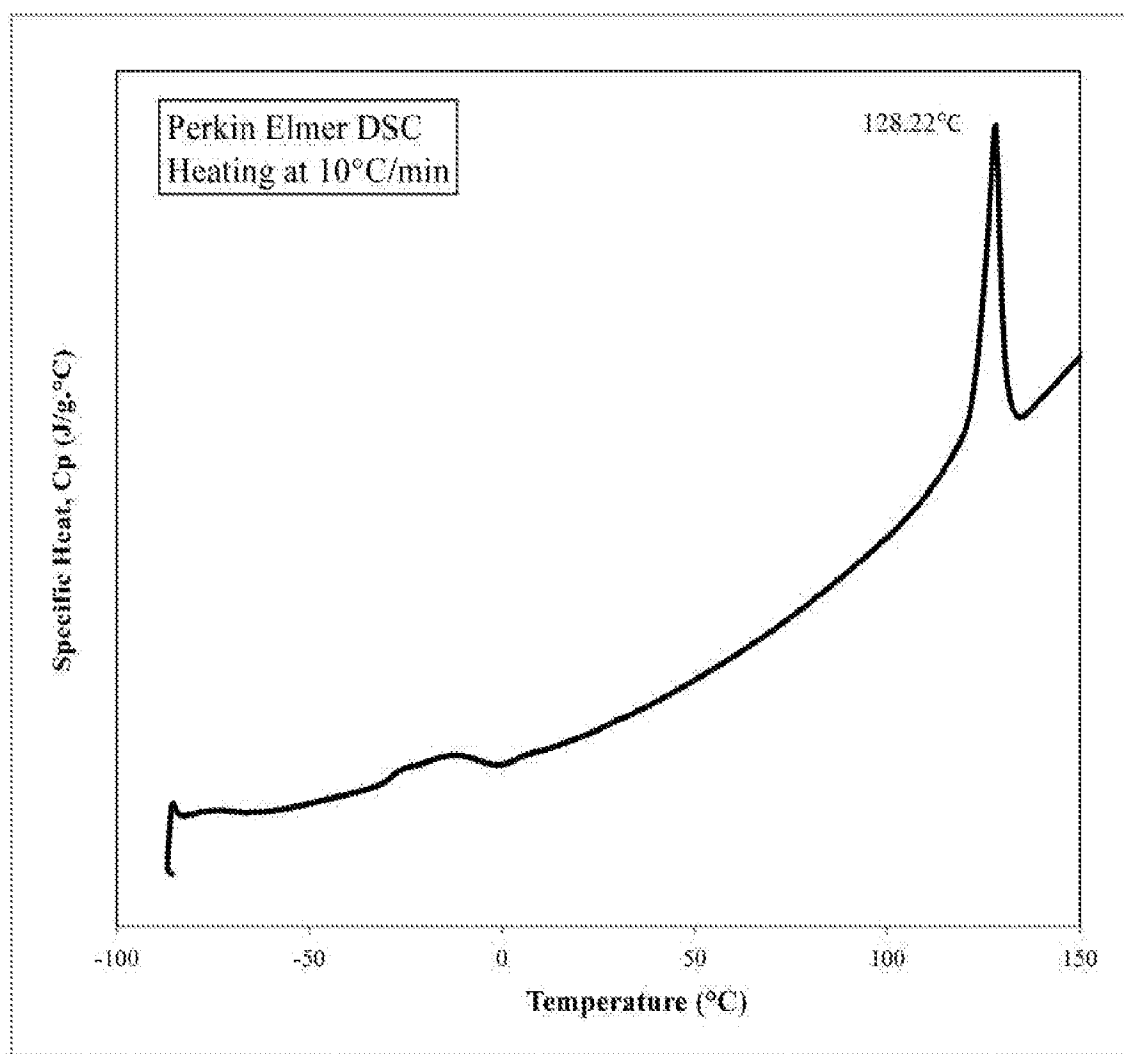


Figure 9

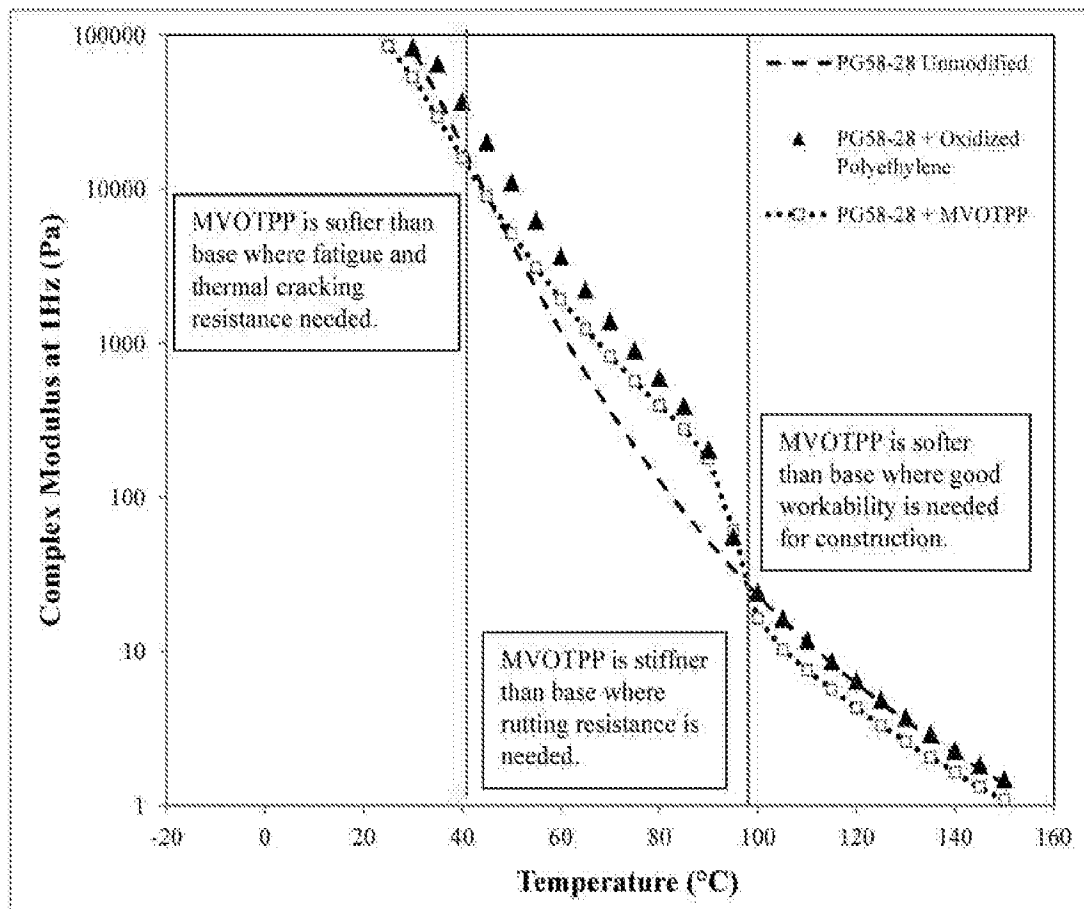


Figure 10

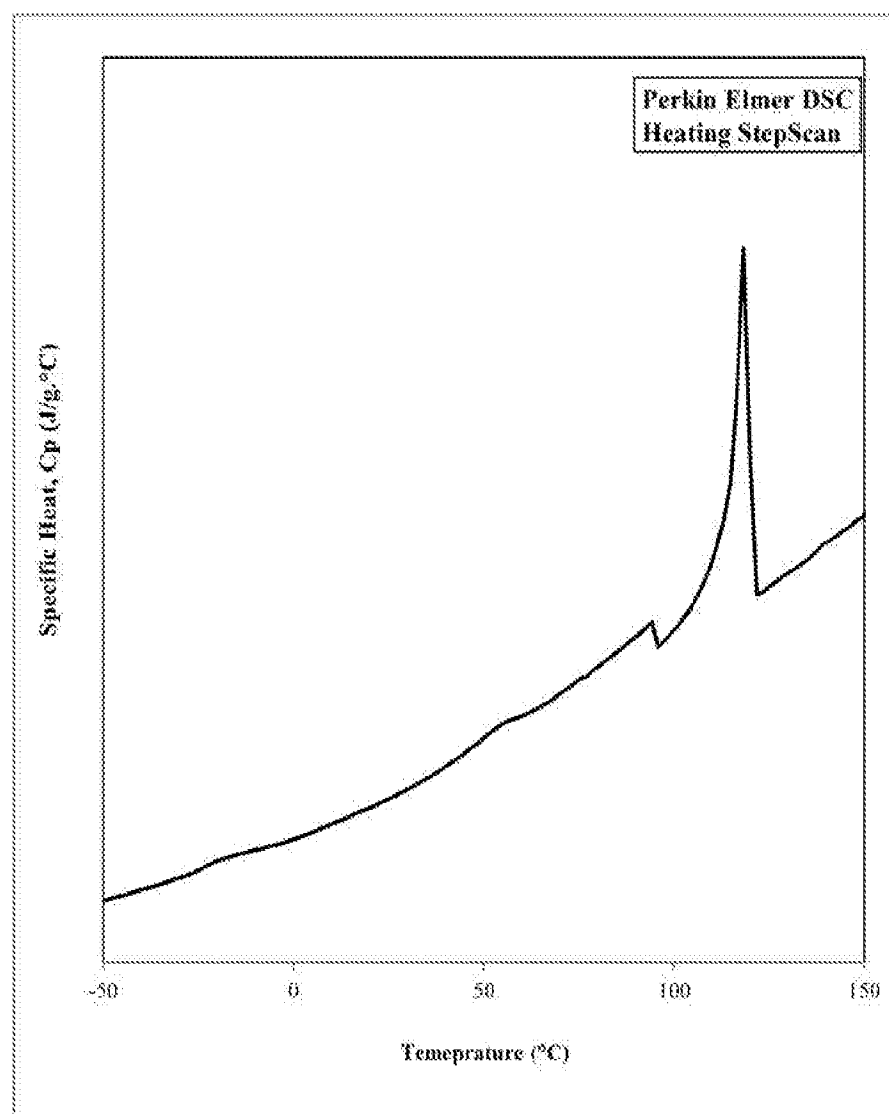


Figure 11

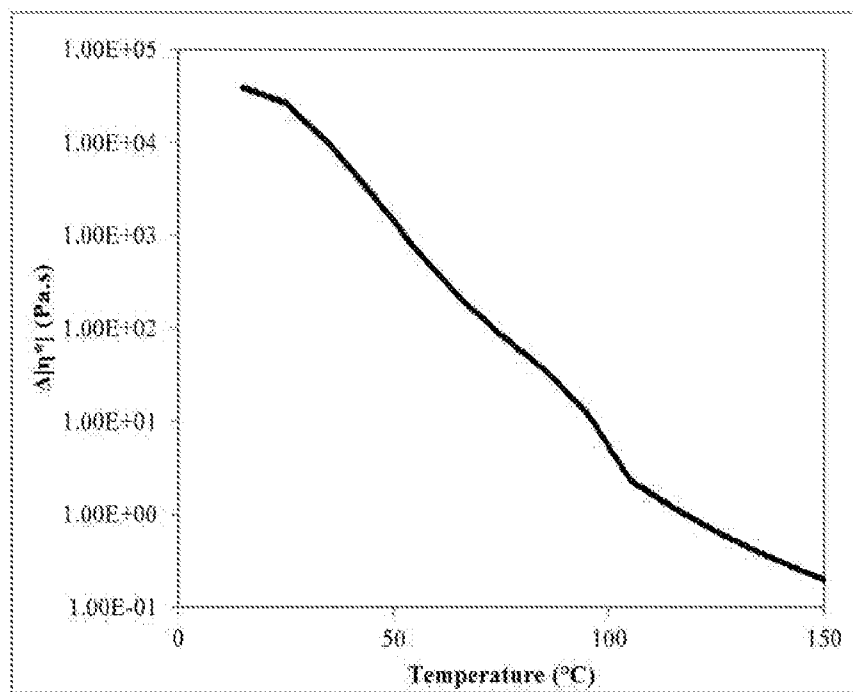


Figure 12

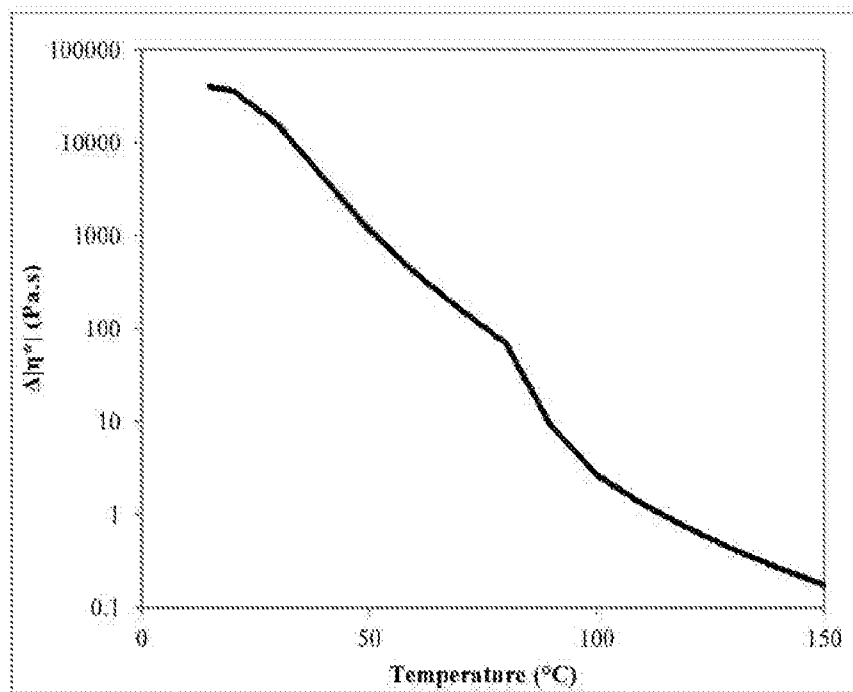


Figure 13

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/034233

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Extra Sheet

Claims 1, 2, 4, 5, 8-13, 16-21 and 24-27 have been analyzed according to the restriction that the claims read upon a polymeric composition, comprising a random copolymer comprising three distinct monomers, wherein a first monomer is a biorenewable oil, wherein the biorenewable oil has been cationically polymerized using Bronsted acids and Lewis acids, wherein the biorenewable oil is plant-based and is recovered corn oil, and a second monomer is a thermoplastic polymer, wherein the thermoplastic polymer is an elastomer, wherein the elastomer is ground tire rubber; and the third monomer is sulfur; and polymeric compositions thereof; and modified asphalt thereof.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1, 2, 4, 5, 8-13, 16-21, 24-27

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/034233

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - C08L 95/00; C08F 293/00; C08L 7/00; C08L 9/00; C08L 91/00; E01C 7/26 (2016.01) CPC - C08L 95/00; C08F 293/00; C08L 7/00; C08L 9/00; C08L 91/00; E01C 7/26 (2016.08) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC - C08F 293/00; C08L 7/00; C08L 9/00; C08L 91/00; C08L 95/00; E01C 7/26 CPC - C08F 293/00; C08L 7/00; C08L 9/00; C08L 91/00; C08L 95/00; E01C 7/26 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC - 428/489; 524/1; 524/59; 524/62; 524/68; 524/71; IPC - C08F 293/00; C08L 7/00; C08L 9/00; C08L 91/00; C08L 95/00; E01C 7/26 CPC - C08F 293/00; C08L 7/00; C08L 9/00; C08L 91/00; C08L 95/00; E01C 7/26 (keyword delimited) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Orbit, Google Patents, Google Search terms used: random, copolymer, thermoplastic, polymer, plastomer, elastomer, ground, tire, rubber, biorenewable, corn, soybean, palm, sunflower, peanut, animal, oil, recover, sulfur, asphalt, tar, pitch, blacktop, bitumen, modifier, monomer, bronsted, lewis, acid, cationic, polymerization		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013/0184383 A1 (IOWA STATE UNIVERSITY RESEARCH FOUNDATION, INC) 18 July 2013 (18.07.2013) entire document	1, 2, 4, 5, 8-13, 16-21, 24-27
A	US 5,360,849 A (BRAGA et al) 01 November 1994 (01.11.1994) entire document	1, 2, 4, 5, 8-13, 16-21, 24-27
A	US 2008/0281071 A1 (IONESCU et al) 13 November 2008 (13.11.2008) entire document	1, 2, 4, 5, 8-13, 16-21, 24-27
A	LU et al. Soybean oil-based, aqueous cationic polyurethane dispersions: Synthesis and properties. Progress in Organic Coatings. Vol. 69, No. 1. September 2010. [retrieved on 25 August 2016]. Retrieved from the Internet. <URL: http://www.sciencedirect.com/science/article/pii/S0300944010001268 >. pp. 31-37	1, 2, 4, 5, 8-13, 16-21, 24-27
A	LU et al. Preparation and properties of starch thermoplastics modified with waterborne polyurethane from renewable resources. Polymer. Vol. 46, No. 23. 14 November 2005. [retrieved on 25 August 2016]. Retrieved from the Internet. <URL: http://www.sciencedirect.com/science/article/pii/S0032386105012073 >. pp. 9863-9870	1, 2, 4, 5, 8-13, 16-21, 24-27
A	US 4,412,019 A (KRAUS) 25 October 1983 (25.10.1983) entire document	1, 2, 4, 5, 8-13, 16-21, 24-27
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 15 September 2016		Date of mailing of the international search report 21 OCT 2016
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300		Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/034233

Continued from Box No. III Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I+: claims 1-41 are drawn to polymeric compositions and modified asphalt thereof.

Group II: claims 42-92 and are drawn to methods thereof.

The first invention of Group I+ is restricted to a polymeric composition, comprising a random copolymer comprising three distinct monomers, wherein a first monomer is a biorenewable oil, wherein the biorenewable oil has been cationically polymerized using Bronsted acids and Lewis acids, wherein the biorenewable oil is plant-based and is recovered corn oil, and a second monomer is a thermoplastic polymer, wherein the thermoplastic polymer is an elastomer, wherein the elastomer is ground tire rubber; and the third monomer is sulfur; and polymeric compositions thereof; and modified asphalt thereof. It is believed that claims 1, 2, 4, 5, 8-13, 16-21, and 24-27 read on this first named invention and thus these claims will be searched without fee to the extent that they read on the above embodiment.

Applicant is invited to elect additional formula(e) for each additional compound to be searched in a specific combination by paying an additional fee for each set of election. Each additional elected formula(e) requires the selection of a single definition for each compound variable. An exemplary election would be a polymeric composition, comprising a random copolymer comprising three distinct monomers, wherein a first monomer is a biorenewable oil, wherein the biorenewable oil has been cationically polymerized using Bronsted acids and Lewis acids, wherein the biorenewable oil is plant-based and is recovered corn oil, and a second monomer is a thermoplastic polymer, wherein the thermoplastic polymer is an elastomer, wherein the elastomer is ground tire rubber; and the third monomer is a vinylaromatic compound; and polymeric compositions thereof; and modified asphalt thereof. Additional formula(e) will be searched upon the payment of additional fees. Applicants must specify the claims that read on any additional elected inventions. Applicants must further indicate, if applicable, the claims which read on the first named invention if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched/examined.

The inventions listed in Groups I+ and II do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I+, polymeric compositions and modified asphalt thereof, are not present in Group II; and the special technical features of Group II, methods, are not present in Group I+.

The Groups I+ and II formulae do not share a significant structural element requiring the selection of alternatives for the monomers, biorenewable oil and thermoplastic polymer.

The Groups I+ and II share the technical features of a polymeric composition, comprising a random copolymer comprising three or more distinct monomers, wherein a first monomer is a biorenewable oil and a second monomer is a thermoplastic polymer; a polymeric composition, comprising a biorenewable oil and a thermoplastic polymer, wherein the thermoplastic polymer comprises about 1-75 wt% of the polymeric composition with a remaining balance of a biorenewable oil; and a modified asphalt, comprising: an asphalt binder in an amount ranging from about 60-99.9 wt%; an asphalt modifier in an amount ranging from about 0.1-40 wt%; wherein the asphalt modifier comprises: about 1-75 wt% of a thermoplastic polymer and a remaining balance of biorenewable oil. However, these shared technical features do not represent a contribution over the prior art.

Specifically, "Soybean oil-based, aqueous cationic polyurethane dispersions: Synthesis and properties" to Lu et al. teach a polymeric composition (Abstract; Pg. 33, Scheme 1), comprising a copolymer comprising three distinct monomers (Pg. 32, 2.2. Synthesis of soybean oil-based, aqueous cationic polyurethane dispersions), wherein a first monomer is a biorenewable oil (Pg. 33, Scheme 1, MSOL) and a second monomer (Pg. 33, Scheme 1, MDI and NMDA); and use of copolymers for ductile plastics (Abstract).

Additionally, "Preparation and properties of starch thermoplastics modified with waterborne polyurethane from renewable resources" to Lu et al. teach a polymeric composition (Abstract), comprising a random copolymer (Pg. 9866, random copolymers...; the polymers prepared by Lu et al. are prepared using the same method as the styrene-co-maleic anhydride random copolymers) comprising distinct monomers, wherein a first monomer is a biorenewable oil (Pg. 9864, 2.3. Extrusion processing, dried starch...) and a second monomer is a thermoplastic polymer (Pg. 9864, 2.2 Preparation of polyurethane dispersion based on castor oil, castor oil...); and a polymeric composition (Abstract), comprising a biorenewable oil and a thermoplastic polymer, wherein the thermoplastic polymer comprises about 1-75 wt% of the polymeric composition (Pg. 9864, 2.2 Preparation of polyurethane dispersion based on castor oil, castor oil...) with a remaining balance of a biorenewable oil (Pg. 9864, 2.3. Extrusion processing, dried starch...);

Additionally, US 4,412,019 A to Kraus teaches a modified asphalt (Abstract), comprising: an asphalt binder in an amount ranging from about 60-99.9 wt% (Col. 4, Table 1, Run 2, Asphalt); an asphalt modifier in an amount ranging from about 0.1-40 wt% (Col. 4, Table 1, Run 2, hydrogenated Rubber); wherein the asphalt modifier comprises: about 1-75 wt% of a thermoplastic polymer (Col. 3, Lns. 53-64, Solprene® 512, a substantially linear butadiene/styrene teleblock polymer coupled with an epoxidized soybean oil...).

The inventions listed in Groups I+ and II therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.